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COLOUR MEASUREMENT.

By E. B. Evans (Fellow), C. F. McCue (Assoc. Fellow), and W. A. Woodrow (Fellow).

Summary.

After reviewing some of the fundamental principles of colour vision and colour measurement, the report deals with the specification of colour by means of the tristimulus equation. This leads to a consideration of the unit trichromatic equation, the chromaticity diagram, and finally the X, Y, Z equation of the C.I.E. System. Methods of colour measurement used in the petroleum and allied industries are then discussed, and some details are given of attempts to correlate results obtained on different instruments. The report ends with a glossary of terms.

Preface.

This report was originally intended to assist members of the Colour Panel of Standardization Sub-Committee No. 3 in their task of co-ordinating methods at present in use in the industry and of making recommendations, particularly regarding the advisability of adopting the C.I.E.* system of colour specification. It was subsequently felt, however, that the subject was of sufficient interest and importance to justify publication.

The theoretical sections of the report are based on "The measurement of colour," by W. D. Wright (Hilger, 1944), to which readers are referred for further information. The glossary consists almost entirely of extracts from a much more comprehensive list published by the Physical Society ("Report on colour terminology, 1948"), to whom acknowledgment is due for permission to copy.

Colour Vision.

Introduction.

The subjective evaluation by the eye of the quality of light which is called "colour" depends not only on the nature of the light falling on the retina but also on the response of the various nerve cells, etc., in the retina and the interpretation which the brain gives to the signals which these cells send to it. Thus, the subject of colour vision is not simply a problem of physics but has also its histological, physiological, and even psychological aspects. Although these aspects are not dealt with as such in the present report it is important to realize that they play their part in all colour vision and so cannot be ignored.

The Nature of Light.

The small band of electro-magnetic radiations which have wavelengths between $0{\cdot}40 \times 10^{-3}$ mm and $0{\cdot}75 \times 10^{-3}$ mm is capable of stimulating the human eye and is known as light.

The sensation produced by light of a certain wavelength falling on the

* Commission Internationale de l'Eclairage (1931); also known in U.S.A. as I.C.I. (International Commission on Illumination).

retina depends to some degree on the conditions of observation, but under normal conditions the shorter wavelengths give a sensation of violet or blue while the longer wavelengths give reds. Between these two limits there are, literally, "all the colours of the rainbow." The main colours recognized in the complete range (known as the continuous spectrum) are usually given as red, orange, yellow, green, blue, indigo, and violet, but it is important to realize that these do not correspond to any specific "steps" up or down the wavelength scale and that the wavelength range allocated to each colour sensation is thus somewhat arbitrary. One such allocation (due to Abney) is given as :—

Colour.	Wavelength range, μ (= 10^{-3} mm).
Red	End–0·62
Orange	0·62 –0·592
Yellow	0·592–0·578
Green	0·578–0·500
Blue	0·500–0·464
Indigo	0·464–0·446
Violet	0·446–end

Every conceivable colour can be analysed as a mixture of radiations of various wavelengths, the relative and absolute amounts of each wavelength determining the nature of the colour. Thus, a colour can be completely specified by its "energy distribution curve" (*i.e.*, a curve showing the amount of energy corresponding to each wavelength).

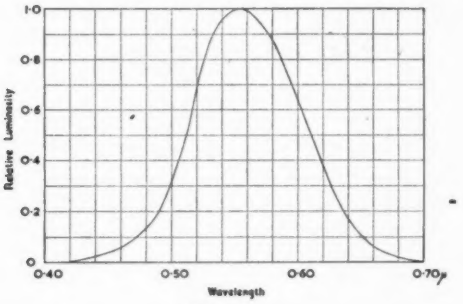

FIG. 1.

THE EQUAL-ENERGY LUMINOSITY CURVE.

The human eye, however, is not equally sensitive to all parts of the spectrum. Yellow light appears much "brighter" than, say, red or blue light of the same energy. The spectral sensitivity curve (visibility or luminosity curve as it is generally called) may be obtained by recording the energy required at each wavelength to produce a visual response of constant magnitude and plotting the inverse of this energy against the corresponding wavelength. The result for fairly high intensities is given in Fig. 1, which shows that the normal eye has maximum sensitivity at 0·555 μ (*i.e.*, yellow-green).

The unit of light flux is the lumen, which is defined as the amount of light emitted per unit solid angle by a point source of one candle-power. Experimental determination of the relation between energy and light flux gives a value of 650 lumens per watt for radiations of wavelength 0·555 μ. Since this is the wavelength of maximum luminosity, the light flux per watt for any other wavelength may be obtained by multiplying 650 by the relative luminosity for that wavelength.

Absorption.

If a beam of monochromatic light travelling through a medium has intensity (or "candle-power") I_0 at A and I at B, where $AB = l$ (Fig. 2), then the ratio I/I_0 is independent of the intensity of the incident light (*i.e.*, if I_0 is doubled so also will be I). This is known as Lambert's law. The ratio I/I_0 is known as the transmission or "brightness" factor and is given by $I/I_0 = e^{-al}$, where e is the base of natural logs and a is a constant depending on the medium and known as the absorption coefficient of the substance.

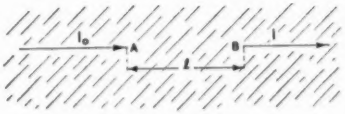

FIG. 2.

Another term widely used in connexion with the absorption of light by a medium is that of optical density, d, which is defined by the equation $d = \log_{10} I_0/I$ ($d = \log_{10} 1/T$ when T = transmission factor). This is a particularly convenient measure of the absorption of a medium because, when the light travels through several absorbing substances, the overall optical density is equal to the sum of the individual densities.

Beer's law states that the absorption is directly proportional to the number of molecules of absorbing substance through which the light passes. Thus, if an absorbing substance is dissolved in a non-absorbing medium, the absorption will be proportional to the concentration. This may be expressed by the equation $I = I_0 \alpha^{-lc}$, where α is a constant for the absorbing substance and c is the concentration (when c and l are both unity: $\alpha = I_0/I$).

In general the transmission factor ($T = I/I_0$) will depend on the wavelength of the incident light, and by plotting T against the corresponding value of λ we obtain the "transmission curve" of the medium. Fig. 3 shows three such curves representing different concentrations of a fictitious dye. If light consisting of an equal amount of energy at all wavelengths is passed through the most concentrated of these solutions, all light wavelengths greater than 0·5 μ (*i.e.*, all except the blue, indigo, and violet) will be almost completely absorbed and the remainder of the spectrum considerably reduced in intensity so that the emergent beam will be a dull indigo or violet. Had the light been filtered through the least concentrated solution, the emergent beam would have contained not only considerably more blue and violet light but also more green, yellow, and red,

so that it would have appeared both brighter and more diluted on account of the admixture of white light. Such a "diluted" colour is described as being "desaturated." A colour free from admixture with white light is said to be "saturated" or (in the U.S.A.) to have a high "chroma."

A medium which absorbs light of all wavelengths to an equal degree is said to be "neutral." Extreme cases of such media are those which do not absorb an appreciable amount of any wavelength (these are said to be "transparent") and those which do not transmit light at all ("opaque" media).

Reflection.

When light is reflected from a surface it is subject to the same changes as those considered above with reference to transmissive absorption. It will be reduced in intensity to some extent, and the ratio of the amount

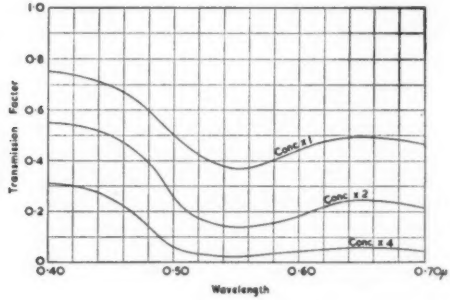

FIG. 3.

TRANSMISSION CURVES OF A SOLUTION FOR RELATIVE CONCENTRATIONS OF 1, 2, AND 4.

of light reflected by the surface to that incident upon it is known as the reflection factor for the wavelength under consideration. If this factor is the same for all wavelengths the surface will appear neutral or grey (ranging from white for 100 per cent reflection to black for zero reflection). If the reflection factor is not constant for all wavelengths (*i.e.*, if the surface reflects certain wavelengths more strongly than others) then a beam of white light will appear coloured on reflection, and a reflection curve for the surface can be plotted in precisely the same way as the transmission curve for a filter.

For most surfaces the percentage of light reflected will depend on the angles of illumination and of viewing. Unless otherwise stated, measurements are made with the incident light making an angle of 45° with the surface, which is then viewed normally.

Sources of Illumination.

The quality of the light transmitted or reflected by a body depends not only on the characteristics of the body but also on the quality of the incident light. For this reason it is necessary accurately to specify the sources of illumination to be used for colour measurement.

The most common way of making a body emit light is to heat it. If the body is a perfect radiator * the energy radiated per unit area of its surface will have a definite magnitude and a definite distribution through the spectrum depending only on the temperature of the body. This is the basis of the "colour temperature" method of specifying a source. The statement that the sun has a colour temperature of about 5000° K means that the quality of sunlight is the same as the light radiated by a perfect radiator heated to a temperature of 5000° K. Similarly the colour temperature of a gas-filled electric lamp is about 2900° K and that of the north sky is about 15,000° K or even higher. The energy distribution curves of these three sources are shown in Fig. 4 (*a*).

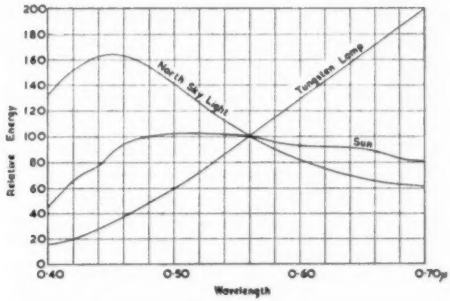

FIG. 4 (*a*).

ENERGY DISTRIBUTION CURVES FOR A GAS-FILLED TUNGSTEN LAMP, THE SUN, AND NORTH SKY LIGHT.

Three standard illuminants are recognized. The first, S_A, represents an average artificial illuminant and is a gas-filled tungsten lamp operated at a colour temperature of 2848° K. The other two, S_B and S_C, represent average daylight in Britain and in America respectively and consist of S_A used in conjunction with suitable filters to give colour temperatures of 4800° K and 6500° K. Fig. 4 (*b*) shows the distribution of the energy radiated by these three sources. The symbol S_E is used to denote a source giving uniform radiation of energy throughout the spectrum. Filters have been produced which give a good approximation to an equal-energy source, but S_E is not an officially recognized illuminant.

COLOUR MEASUREMENT.

The Trichromatic System.[1, 2]

It has been found experimentally that any colour can be matched by mixing appropriate amounts of three suitably chosen stimuli. The basic stimuli or "additive primaries" as they are called are usually a red, a green, and a blue, and the C.I.E. have selected wavelengths of 0·700 μ, 0·5461 μ,

* A perfect radiator is also a perfect absorber. Hence, when at room temperature, it will absorb all radiations incident on it and so appear black. For this reason a perfect radiator is sometimes referred to as a "black body."

and 0·4358 μ for this purpose. If we denote the primaries by the symbols R, G, and B, and the colour to be matched by C, then C can be expressed algebraically by the equation $cC = uR + vG + wB$, where c, u, v, and w are the amounts of C, R, G, and B respectively as measured in some convenient unit. Now, since when neither red nor green nor blue predominates, the result is white light, it is reasonable to adopt the convention that the amounts of R, G, and B shall be regarded as equal when their mixture matches the equi-energy source (*i.e.*, $sS_E = 1{\cdot}0R + 1{\cdot}0G + 1{\cdot}0B$, where s represents the number of units of S_E produced by mixing one unit each of R, G, and B). If, furthermore, the unit quantity of C is defined as the amount of C represented by the equation whose R, G, B coefficients add up to unity, the above equation becomes: $1{\cdot}0C = rR + gG + bB$ (where $r + g + b = 1$). This is known as the unit trichromatic

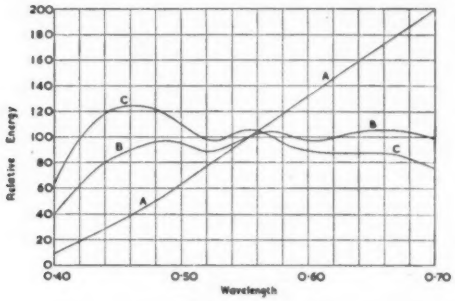

FIG. 4 (*b*).

ENERGY DISTRIBUTION CURVES FOR SOURCES A, B, AND C.

equation and the amount of C represented by it is known as one trichromatic unit (or one T unit). The equation for one T unit of white light will be seen to be $S_E = 0{\cdot}333R + 0{\cdot}333G + 0{\cdot}333B$.

The Chromaticity Diagram.

Since in the unit trichromatic equation $r + g + b = 1$, if r and g are known, b can be found from $b = 1 - (r + g)$. Thus, the quality of a colour is fixed by two quantities and can therefore be represented graphically on a plane diagram having rectangular axes representing r and g respectively. On such a diagram the co-ordinates of S_E would be (0·333; 0·333) and those of the three primaries R, G, and B would be (1·0; 0); (0; 1·0) and (0; 0) respectively. From the geometry of the diagram the line RG (Fig. 5) represents the locus of points for which $r + g = 1$, *i.e.*, colours consisting of mixtures of red and green with no blue, going from red through orange and yellow to green. Similarly, BG is the locus of blue-greens, and BR is the locus of purples. Points inside the triangle RGB represent colours containing all three primaries, that is to say desaturated colours.

Colour Mixture.

If one trichromatic unit of colour C_1 which is represented by $C_1 = r_1R + g_1G + b_1B$ ($r_1 + g_1 + b_1 = 1$) is mixed with an equal amount of

C_2, where $C_2 = r_2R + g_2G + b_2B$ $(r_2 + g_2 + b_2 = 1)$, the resultant colour C_3 will be represented by $2C_3 = (r_1 + r_2)R + (g_1 + g_2)G + (b_1 + b_2)B$. The unit equation for C_3 will therefore be $C_3 = r_3R + g_3G + b_3B$, where $r_3 = (r_1 + r_2)/2$; $g_3 = (g_1 + g_2)/2$; $b_3 = (b_1 + b_2)/2$.

From simple geometrical considerations it follows that, graphically, C_3 must lie on the straight line joining C_1 and C_2 and midway between them.

Similarly it may be shown that if m units of C_1 are mixed with n units of C_2 the resulting colour will be $(m + n)$ units of C_3 where $C_1C_3/C_3C_2 = n/m$.

Thus the new colour is located at the centre of gravity of two weights of masses m and n placed at C_1 and C_2 respectively. This principle can

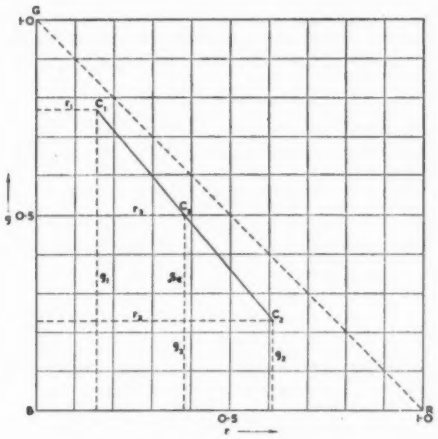

FIG. 5.

CHROMACITY DIAGRAM FOR R, G, B STIMULI.

be extended to mixtures of three or more colours, a special case being the mixture of equal amounts of R, G, B to give white, located at the centre of gravity of three equal weights placed at R, G, and B. From the same principle it follows that any colour produced by the mixture of positive amounts of R, G, and B must lie within the triangle RGB.

The Spectrum Locus.

Fig. 6 represents the locus of the spectral colours plotted on the RGB diagram. It will be seen that, except for the primaries themselves, it lies outside the triangle RGB. Thus, spectral blue-green (for example) of wavelength 0·50 μ can be matched only by a mixture of B and G with a *negative* amount of R. This means in practice that the spectral blue-green is first desaturated by addition of a known amount of R, and the resulting colour is then matched with R, G, and B. If r' units of R are added to the spectral colour and r'', g, and b are the amounts of R, G,

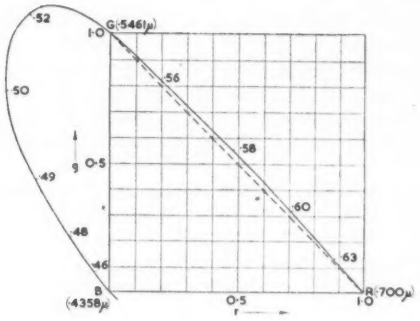

FIG. 6.

SPECTRUM LOCUS PLOTTED ON R, G, B CHROMATICITY DIAGRAM (VERY APPROXIMATE).

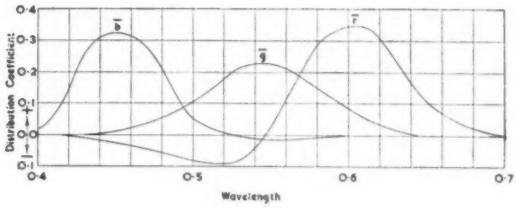

FIG. 7.

DISTRIBUTION COEFFICIENTS OF R, G, B THROUGH THE EQUAL-ENERGY SPECTRUM.

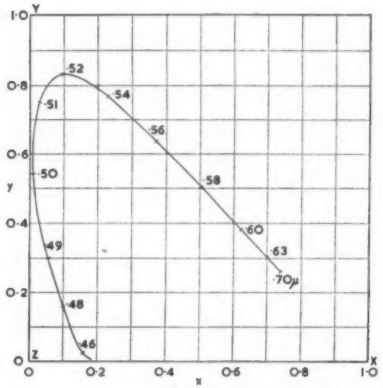

FIG. 8.

SPECTRUM LOCUS ON X, Y, Z SYSTEM.

and B then required for a match we have $C + r' R = r''R + gG + bB$, or $C = gG + bB - rR$ where $r = r' - r''$.

Fig. 7 shows the relative amounts of R, G, and B (measured in T units) through the equi-energy spectrum. These amounts (designated $\bar{r}$, $\bar{g}$, $\bar{b}$) are known as the distribution coefficients.

The XYZ *Co-ordinates.*

By suitably shifting the axes the spectrum locus shown in Fig. 6 can be transformed to that of Fig. 8. Here, instead of R, G, and B, the reference points are designated X, Y, and Z. These are the imaginary stimuli chosen by the C.I.E. in order that :—

(i) The spectrum locus (and hence every real stimulus) lies entirely within the triangle XYZ,

(ii) The straight part of the spectrum locus (*i.e.*, the red to greenish-yellow portion) coincides with the line XY,

(iii) X and Z have zero luminosity.

The first clause ensures that all coefficients of tri-stimulus equations will be positive; the second enables a large part of the spectrum to be expressed in terms of X and Y only, and the third clause means that the luminosity of $1T$ unit of the matched colour is given by yL_T, where y is the coefficient of Y in the unit trichromatic equation, and L_T is the luminosity of $1T$ unit * of Y which is defined as unity.

It must be emphasized that X, Y, and Z do *not* represent real stimuli and are best regarded as convenient mathematical abstractions.

TABLE I.

Wavelength. μ.	$\bar{x}$.	$\bar{y}$.	$\bar{z}$.
0·38	0·0014	0·0000	0·0065
0·40	0·0143	0·0004	0·0679
0·42	0·1344	0·0040	0·6456
0·44	0·3483	0·0230	1·7471
0·46	0·2908	0·0600	1·6692
0·48	0·0956	0·1390	0·8130
0·50	0·0049	0·3230	0·2720
0·52	0·0633	0·7100	0·0782
0·54	0·2904	0·9540	0·0203
0·56	0·5945	0·9950	0·0039
0·58	0·9163	0·8700	0·0017
0·60	1·0622	0·6310	0·0008
0·62	0·8544	0·3810	0·0002
0·64	0·4479	0·1750	0·0000
0·66	0·1649	0·0610	0·0000
0·68	0·0468	0·0170	0·0000
0·70	0·0114	0·0041	0·0000
0·72	0·0029	0·0010	0·0000
0·74	0·0007	0·0003	0·0000
0·76	0·0002	0·0001	0·0000
Total	5·3456	5·3489	5·3264

* Trichromatic units on the XYZ system are defined in the same way as on the RGB system, viz : $S_E = 1/3\ X + 1/3\ Y + 1/3\ Z$ and $1{\cdot}0C = xX + yY + zZ$, where $x + y + z = 1$. Thus $1\ T$ unit on the XYZ system will represent an amount different from $1\ T$ unit on the RGB system.

Table I gives the distribution coefficients at 0·02 μ intervals through the equi-energy spectrum. These are plotted graphically in Fig 9. It will be observed that the totals of $\bar{x}$, $\bar{y}$, and $\bar{z}$ are substantially equal. This is in accordance with the convention that the amounts of the three stimuli present in a match for an equi-energy source are regarded as equal. Further, it will be seen that the curve for $\bar{y}$ in Fig. 9 is precisely the same as the luminosity curve shown in Fig. 1. This is due to the fact that X and Z have zero luminosity, and hence the luminosity of a colour is entirely a function of its coefficient of Y.

Dominant Wavelength and Excitation Purity.

From the deductions already made concerning the mixture of two colours in the chromaticity chart, it follows that, if S is a point repre-

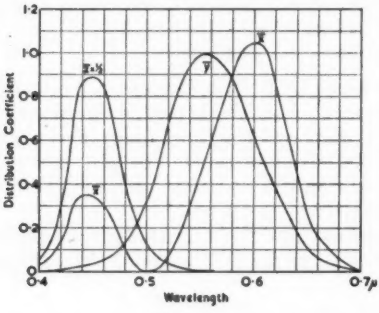

FIG. 9.

DISTRIBUTION COEFFICIENTS OF X, Y, Z THROUGH THE EQUAL-ENERGY SYSTEM.

senting any one of the standard illuminants S_A, S_B, S_C, or S_E and C represents a given colour and if a line drawn from S through C intercepts the spectrum locus at wavelength λ (see Fig. 10), then C would be matched in quality by mixing monochromatic light of wavelength λ with white light in the ratio of CS to $C\lambda$. Thus, colour quality can be specified in terms of its "dominant wavelength" and its "excitation purity" which is defined as the ratio $CS/\lambda S$. It will be observed that the excitation purity of white light is zero, while that for spectral colours is unity.

Because of the gap in the spectrum locus, a special convention has to be adopted for points such as C_1 which lie in the purple segment of the chromaticity chart. These are defined by reference to the "complementary" wavelength (*i.e.*, the wavelength which when mixed with the given colour produces white light) found by producing C_1S to meet the spectrum locus at λ_c. The excitation purity, on the other hand, is defined as the ratio C_1S/PS, where P is the point of intersection of SC_1 produced and the straight line joining the extremities of the spectrum locus.

COLORIMETERS.

Instruments for measuring or comparing colours may be roughly divided into four classes: (1) comparative instruments of limited range, (2) tri-

chromatic colorimeters, (3) spectrophotometers, and (4) photo-electric instruments. In the following paragraphs the colorimeters used in the petroleum industry are considered under these headings, and the section ends with a description of some work which has been carried out by the Colour Panel of the I.P. in an attempt to correlate results obtained on different instruments.

(1) *Comparative Instruments of Limited Range.*

These instruments are designed for a specific purpose (*e.g.*, for use with petroleum products) and usually consist of a means of comparing the colour of light transmitted by a layer of the sample with that transmitted by standard glasses. Broadly speaking, there are two types differentiated by the method of obtaining a match: (*a*) those in which

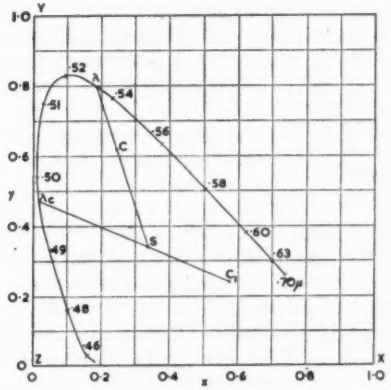

FIG. 10.

COLOUR SPECIFICATION ON THE MONOCHROMATIC-PLUS-WHITE BASIS.

the depth of sample is adjusted and (*b*) those in which different matching standards are used. Of the instruments described below (i) to (vi) are of type (*a*) and the remainder type (*b*); numbers (i), (ii), (vii), and (viii) are widely used, (ix) is of limited application, and the remainder are practically obsolete.

Results obtained on these instruments are usually expressed in arbitrary units which are not readily convertible to universally recognized units such as the C.I.E. system. This system can, however, be used to specify the nature of the standard glasses, while the illuminant is usually specified in terms of its colour temperature.

(i) *The Saybolt Chromometer* (A.S.T.M., D156-38; I.P.18/42) is intended for use with refined oils such as motor fuel and kerosine. The sample is contained in a graduated tube fitted with a tap so that the depth of oil may be adjusted until its colour matches a standard disc or discs viewed through a similar but empty tube. The two colours appear in adjacent halves of a circular field. The light source, which illuminates

both oil and disc(s), consists of a 60-W lamp (of colour temperature 2750° K) in combination with a filter whose characteristics are defined by limiting values for the co-ordinates on the C.I.E. system and for its luminous transmission. This combination yields an approximation to daylight which is intermediate in quality between Standard Illuminants B and C.

The depth of oil required for a match is converted by means of Tables to an arbitrary "Saybolt Colour." Diller *et al.*[5] state that this is primarily a measure of saturation (or "chroma") rather than luminous transmission.

(ii) *The Tag–Robinson Colorimeter* ("Tag manual," C. J. Tagliabue Mfg Co.) is chiefly for use with lubricating oils. The sample is contained in a glass-bottomed brass tube into which dips a similar but narrower tube which can be raised or lowered by means of a rack and pinion, thus varying the effective depth of the oil. Three standard glasses are provided; one of these is selected and mounted in a tube similar to that dipping into the sample. Both the oil and the standard glass are illuminated by a lamp similar to that used with the Saybolt instrument, and the two colours are viewed in the two halves of a circular field.

(iii) *Stammer Chromometer*
(iv) *Duboscq Colorimeter*
(v) *Kober Colorimeter*
(vi) *Klett Colorimeter*

All these instruments are similar in principle to the Tag–Robinson. None of them is now much used in the petroleum industry.

(vii) *The Lovibond Tintometer, I.P. Series* (I.P.17/45), is intended for motor fuels, kerosine, gas oils, lubricating oils, petrolata, and paraffin waxes. Comparison is made between the colour of the sample contained in a suitably sized cell (a range from 1/16 to 18 in. is available) and standard glasses arbitrarily numbered from 0 to 4 in intervals of $\frac{1}{4}$. These glasses are defined in terms of their colour matches with Lovibond red (200 series) and yellow (510 series) glasses.

(viii) *The A.S.T.M.–Union Colorimeter* (N.P.A. Colorimeter) (A.S.T.M D155-45T) compares the colour of the sample of lubricating oil or petrolatum contained in a standard test jar with one of a series of glasses mounted in a movable rack, the two colours appearing in neighbouring circular fields. The standard glasses are defined in terms of the Lovibond 200, 510, and 1180 series, and the lamp, which illuminates both the sample and the glasses, is the same as that used in the Saybolt instrument. Results are expressed either on an arbitrary numerical scale (known as A.S.T.M. or N.P.A. colour numbers) or by names such as cream white, orange pale, or claret red.

(ix) *The White Oil Manufacturers Association (W.O.M.A.) Colorimeter* is intended for use with white oils. It consists of two vertically mounted glass tubes illuminated from below by a lamp similar to that used in the Lovibond instrument. The sample is contained in one of the tubes, and its colour is matched by means of standard glasses carried in a circular mounting. The glasses are defined in terms of the Lovibond 200 and 510 series.

(x) *The Wilson Chromometer* is very similar in principle to the W.O.M.A. instrument. Although now almost obsolete it was at one time quite

widely used for measuring colour of refined oils; results were expressed in descriptive terms such as a water white, superfine white, and prime white.

(2) *Trichromatic Colorimeters.*

These are of two distinct types: (*a*) additive and (*b*) subtractive. In the additive types the colour is matched by mixing various amounts of three stimuli (a red, a green, and a blue) in such a manner that they enter the eye simultaneously or in such rapid succession that the eye perceives them as one colour. Subtractive trichromatic colorimeters consist of devices whereby white light is passed through three filters in succession. One of these filters absorbs red light, another absorbs green, and the third blue,* so that by varying the densities of the three filters the amounts of red, green, and blue in the transmitted light may be adjusted to match the light transmitted by the sample.

The additive type gives readings in terms of R, G, and B and, if the characteristics of these three stimuli are known in terms of the C.I.E. system, these readings may be expressed as a tri-stimulus equation in X, Y, and Z.

Subtractive colorimeters do not allow of such simple conversion, but as will be seen below (under "Lovibond–Schofield System") a device may be employed whereby the relative intensity of illumination of the sample and filters may be adjusted so that only two filters are necessary to obtain a match. Use of this device and conversion charts enables readings to be converted to the C.I.E. System.

(i) *The Donaldson Colorimeter* is not used in the petroleum industry, but is included in this report as a typical example of an additive colorimeter of wide application. It employs colour filters to select the red, green, and blue radiations, the intensities of which are controlled by varying the area of each filter through which the light has to pass. Mixture of the three beams is effected by focusing them on the window of an integrating sphere. Within the sphere, which on its inner surface is silver-plated and then covered with a layer of magnesium oxide, the beams suffer repeated diffuse reflections and thus produce a uniform illumination on the surface of the sphere. A second window in the sphere permits the diffused light to emerge and be reflected into a photometer prism for observation in the usual way.

(ii) *The Lovibond Tintometer* is designed on the subtractive principle and uses three series of colour slides, "red," "yellow," and "blue," which are combined to match the sample. The series are made in various values with steps of 0·01 in the lower ranges, 0·1 intermediately, and 0·5 for the higher values. The lowest value slide normally made is 0·01 and the highest 20·0, so that slide values can be obtained to the nearest 0·01. The values of the slides are such that the combination of equal values of the three series absorbs white light and appears as a grey or neutral tint. The results are expressed in terms of the total values of each colour slide needed for matching. If slides of all three series are used in making a

* The filter which absorbs red light (sometimes called the "minus red") transmits blue, green, and, to a lesser extent, yellow, and thus is blue-green or cyan in colour. In fact, it is usually more nearly blue, and so is often referred to merely as "blue." Similarly the "minus green" transmits red and to a lesser extent blue, and so is magenta in colour and commonly referred to as "red," while the "minus blue" is "yellow."

match, the value of the lowest series is deducted from each, and the result reported as the value of each of the remaining colours plus a neutral value; *e.g.*, if the slides used to achieve a match as regards both quality and brightness are 8·0 red, 6·0 yellow, and 2·5 blue, this would be reported as 5·5 red, plus 3·5 yellow, plus 2·5 neutral. Should only two of the three series be required for a match and the sample appear brighter than the standards, neutral tint slides are introduced in front of the sample and the requisite value recorded as " brightness " in addition to the values of the two slides used. Thus, the instrument gives a means of recording both quality and brightness with reference to the particular standards used. The glasses can be taken as additive in respect of colour quality, but a certain loss of brightness occurs in combinations of slides due to scattering of light at the glass surfaces. For this reason the minimum number of slides necessary to give a match should always be employed.

Colours of petroleum products can normally be matched without the use of the " blue " glasses, and so these are omitted in the I.P. Standard Method I.P. 17/45.

(iii) *Lovibond–Schofield System.* The results of measurements on the Lovibond Tintometer are expressed arbitrarily in terms of the particular standard glasses with which the instrument is constructed, and such results cannot be readily converted into terms of other instruments or to the international nomenclature.

To surmount this difficulty the Lovibond–Schofield system [6] has been devised. In this not more than two of the three colour series are employed in matching a particular colour quality, and the relative intensity of the illumination falling on the test material and the matching glasses is controlled by a mechanism in the form of an obturator vane and which is known as the " Rothamsted Device." Neutral-tint glasses are not used with the instrument modified in this way. The standard illuminants of the C.I.E. system are used, involving the use of glass cells fitted with the filter solutions necessary to obtain illuminants B and C. Matches are made in the usual way, recording the values of the slides used and also the scale reading of the obturator vane necessary to obtain a match for brightness (this may be either positive or negative).

Conversion charts have been prepared for each of the standard illuminants so that the C.I.E. colour co-ordinates can easily be obtained graphically. A further graph has been constructed so that the visual density of the Lovibond slides used can be obtained. The obturator-scale reading gives the difference in visual density between the sample and the slide combination. Unless compensating slides of clear glass are introduced on the sample side of the field, a correction must be made to the slide value as obtained from the visual density graph, the correction depending on the number of slides used for the match. From the visual density of the sample obtained by adding the slide value and the vane-scale reading, the brightness factor (relative to magnesium carbonate) can be obtained from the relation,

$$\text{Visual density} = -\log_{10} \text{ Brightness Factor } \%/100$$

From the conversion graphs the dominant hue wavelength and saturation can also be obtained.

(3) *Spectrophotometers.*

The distribution of energy throughout the spectrum is measured either visually or photo-electrically. By comparison of the curve so obtained with the X, Y, Z distribution curves the C.I.E. specification of the colour may be obtained. Energy distribution curves give information which cannot be deduced from the tristimulus specification alone, and since the measurement of amount of energy does not depend on the visual peculiarities of the observer this method is not subject to error from this source. For these reasons it is likely that spectrophotometers (especially photo-electric models) will play an increasing part in colorimetric work in the future.

(4) *Photo-electric Methods.*

In addition to the photo-electric spectrophotometers mentioned above, photo-cells are used to replace the observer in other types of colorimeter. The photo-electric tricolorimeter makes use of three photo-cells; one having a spectral sensitivity curve similar to the $\bar{x}$ distribution curve, the second to the $\bar{y}$ curve, and the third to the $\bar{z}$ curve. Ideally the outputs from these three cells could be amplified and registered on meters calibrated to yield C.I.E. units directly, but in practice it is extremely difficult to obtain cells having exactly the required response curves, and it is more convenient to employ cells of known sensitivity and then convert readings obtained with these to C.I.E. units.

Diller, De Gray, and Wilson [4, 5] have shown that the spectral transmission curves of petroleum products are smooth and of the same general shape, invariably showing greater transmission as the wavelength increases. These findings form the basis of the attempts of the A.S.T.M. to evolve a satisfactory photo-electric colorimeter. In the 1942 Report of Committee D2 [3] there appeared a "Proposed method of test for color of lubricating oil" which employed a closely specified instrument standardized by means of six aqueous solutions. This was superseded in 1947 by a proposed method of wider application using glass filters as standards. Special procedures are necessary for water-white or very dark products, but intermediate "colour indexes" are simply expressed as the percentage of "north sky" light transmitted by a 20-mm layer of the sample. "Abnormal" samples (*i.e.*, those having spectral transmission curves of unusual shape) are detected by measuring their red transmittance and comparing the results with figures quoted for normal oils.

Correlation between Different Types of Instruments.

With so many different types of colorimeter in use it would obviously be very convenient if there were some means of converting readings from one scale to another. Unfortunately, this is not so simple a matter as it may seem at first sight. First, the different instruments employ different sizes of cell, and although normal petroleum products do not exhibit any marked dichroism the hue of a sample does depend to some extent on the thickness of the observed layer. Secondly, the quality of light transmitted by a sample must depend to a large degree on the quality of the

TABLE II.

Colour Determinations by Means of the Lovibond, Lovibond–Schofield, A.S.T.M.–Union, and Tag–Robinson Instruments.

Sample.	Size of cell, Inches.	Lovibond Tintometer.				Lovibond–Schofield system.								A.S.T.M.–Union.	Tag–Robinson.
		Red.	Yellow.	Blue.	Brightness.	Red.	Yellow.	Blue.	Scale reading.	Visual density.		C.I.E. units (Illuminant B).					
										Slides.	Total.	*X.*	*Y.*	*Z.*	Brightness, %.		
1	6	0	1·5	0	0	0	1·5	0	+0·06	0·012	0·072	0·370	0·386	0·244	84·7	—	—
2	6	0	3·3	0	0	0	3·2	0	0	0·022	0·022	0·388	0·419	0·265	95·1	—	—
3	6	0·4	4·0	0	0	0·5	4·1	0	+0·05	0·054	0·104	0·405	0·423	0·179	78·7	—	—
4	6	0	5·5	0	0	0	5·2	0	0	0·035	0·035	0·404	0·443	0·153	92·2	—	—
5	6	0·9	12·0	0	0·1	0·9	12·0	0	0	0·12	0·12	0·446	0·469	0·095	75·8	—	—
6	½	0·4	2·0	0	0	0·3	2·1	0	+0·04	0·032	0·072	0·382	0·396	0·232	84·7	1	11
7	½	2·0	22·0	0	0·5	1·8	22·0	0	0	0·225	0·225	0·476	0·478	0·046	59·5	2	20
8	½	4·3	40·0	0	0	4·4	40·0	0	+0·06	0·428	0·488	0·514	0·461	0·095	32·4	3½	11½
9	½	23·0	60·0	0	0	25·0	70·0	0	+0·05	1·140	1·190	0·634	0·364	0·092	6·5	6	10½
10	½	18·0	40·0	2·1	0	19·0	60·0	0	+0·32	0·970	1·290	0·613	0·384	0·093	5·1	7–8	2
																	11½

light incident on it. Of the instruments in common use, the Saybolt, Tag–Robinson, and A.S.T.M. Union all specify the same illuminant, while the Lovibond instrument employs a slightly different one. Therefore, some correlation is to be expected between the Tag–Robinson and the A.S.T.M.–Union, provided that the depth of oil used in the former approximates to the width of cell used in the latter. Apart from this, there can be no dependable correlation between the various colorimeters. However, the Colour Panel considered that a useful purpose would be served by determining the colour of a number of samples on different instruments and comparing the results. Initially the investigation was restricted to the Saybolt Chromometer and the Lovibond Tintometer (I.P. Series). Twenty samples of gasoline, kerosine, and benzole were examined in nine different laboratories and the results were published in the *Journal* of the Institute.[7] As was to be expected, there was found to be some degree of correlation between the two sets of readings; one non-conforming sample, however, served as a reminder of the inherent impossibility of obtaining a foolproof "conversion factor." This work was later extended to the Trichromatic Lovibond, the Lovibond–Schofield, the A.S.T.M.–Union, and the Tag–Robinson instruments. Measurements were made on kerosines, gas oils, and lubricating oils, and a summary of the results obtained is given in Table II. As explained above, the correlation which was found between the Tag–Robinson and A.S.T.M.–Union instruments was to be expected. There also appears to be some relationship between these results and the "brightness" as measured on the Lovibond–Schofield instrument. Results obtained on the Lovibond Tintometer are more difficult to interpret, as is shown by samples 8, 9, and 10 in particular. The lack of correlation between the Tintometer readings and the "brightness" of samples 1, 2, and 4 also serves to illustrate the complex nature of this problem.

Acknowledgment.

The authors are indebted to Messrs. Hilger & Watts, Ltd., for permission to reproduce Figs. 1, 2, 3, 4 (*a*), 9, and 10 from "The measurement of colour" by W. D. Wright.

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APPENDIX.

Colour Terminology.

The terms and definitions which follow are taken from the Report on Colour Terminology prepared by a Committee of the Colour Group of the Physical Society. The terms preferred by the Committee are printed in CAPITALS and unam-

biguous alternatives in SMALL CAPITALS. Where the term is not considered essential it is printed in lower case type. Deprecated terms are in lower case *italics*. If one of the alternative terms is the most commonly used, it is given first in order to facilitate identification, but otherwise the preferred term is placed first.

TERMS USED IN COLOUR PHYSICS.

The characteristics of radiation, other than its distribution in space and time, are defined by its energy and spectral distribution. One of the properties of radiation, confined to radiation lying within a certain spectral region, is the capacity to stimulate the eye and cause visual sensations. Such radiation is commonly known as light. Apart from differences in spatial distribution and fluctuations with time, the nature of the visual sensations may differ in the quality called colour which, under controlled conditions, is related to the distribution of energy in the spectrum of the light causing the sensations. The study of colour is concerned with this quality of the visual sensations, with the light causing them, and with the source of the light.

A. GENERAL TERMS.

1. LIGHT.

(*a*) Radiant energy capable of stimulating the eye and causing the sensation of vision. Often extended to radiation near to the visible region of the spectrum, *e.g.*, ultra-violet light, infra-red light (deprecated). Light actually entering the eye may be more specifically referred to as the visual stimulus.

(*b*) Visual sensation.

2. COLOUR.

(*a*) That characteristic of the visual sensation which enables the eye to distinguish differences in its quality, such as may be caused by differences in the spectral distribution of the light rather than by differences in spatial distribution or fluctuations with time.

(*b*) As (*a*), but applied directly to the stimulus or the source (primary or secondary) giving rise to the sensation. For brevity the stimulus is often referred to as the colour.

(*c*) That property of an object or stimulus, or quality of a visual sensation, distinguished by its appearance of redness, greenness, etc., in contradistinction to whiteness, greyness, or blackness (*i.e.*, chromatic colour in contradistinction to achromatic colour—see Nos. 21 and 22).

3. SURFACE COLOUR.

The colour of an illuminated surface.

4. ADDITIVE MIXTURE.

The mixture of light stimuli in such a manner that they enter the eye simultaneously or in rapid succession, and are incident on the same area of the retina or enter in the form of a mosaic which the eye cannot resolve.

5. SUBTRACTIVE MIXTURE.

The mixture of absorbing media or the superposition of filters so that the composition of the light stimulus passing through the combination is determined by the simultaneous or successive absorption of parts of the spectrum by each medium present.

6. ADDITIVE PRIMARIES.

Certain dyes, pigments, or other secondary or primary sources of light (*e.g.*, monochromatic radiations) giving rise to stimuli predominantly confined to one part of the spectrum, which by additive mixture of the stimuli in varying proportions can be made to match a large range of colours. Generally three in number, a red, a green, and a blue.

7. SUBTRACTIVE PRIMARIES.

Certain dyes or pigments characterized by strong absorption in one part of the spectrum, which by subtractive mixture in varying proportions can be made to match a large range of colours. Generally three in number, a minus red, a minus green, and a minus blue, *i.e.*, a cyan, a magenta, and a yellow.

8. COMPLEMENTARY COLOURS.

(*a*) Additive.
Any two colours which, by additive mixture, can be made to match an achromatic colour.
(*b*) Subtractive.
Any two absorbing media which, by subtractive mixture, can be made to match an achromatic colour.

9. MINUS COLOURS.

The colour which is complementary (in sense 8 (*a*)) to the colour named, *e.g.*, minus red (cyan) is a colour complementary to red.

10. DICHROISM.

A phenomenon exhibited by certain dyes or pigments, and characterized by a marked change of hue with change in the observing conditions. The chief instances are (*a*) appreciable change of hue with change in the colour temperature of the illuminant, and (*b*) appreciable change of hue with change in the concentration or thickness of the dye or pigment layer.

B. PHOTOMETRIC TERMS.

Light is measured by comparing it with that derived from a physically defined source, equality in the amount of light from the test stimulus and the standard source being judged by equality in the magnitude of the visual sensations. Thus, whereas in radiometry the stimulus is completely defined in terms of radiant flux (watts) and spectral distribution, in photometry it is defined in terms of luminous flux (lumens) and spectral distribution. In visual comparisons the luminance is usually a more convenient measure of the stimulus than the luminous flux.

11. PRIMARY LIGHT SOURCE.

A body or object emitting light by virtue of a transformation of energy into radiant energy within itself.

12. SECONDARY LIGHT SOURCE.

A body or object transmitting or reflecting light falling on it from any other source (primary or secondary).

For the sake of brevity in this Report this term is held to include all objects which can modify the spectral distribution of the light, such as filters and mirrors, although strictly there would be objection to referring to these as secondary sources. A secondary source is thus an object or body the colour of which depends on the illuminant. The object or body may be diffusely or directly reflecting or transmitting, and these properties may occur wholly or partially in any combination.

13. EQUAL ENERGY SOURCE.

A light source from which the amount of energy radiated is constant for the same wavelength interval throughout the visible spectrum.

14. FULL RADIATOR. *Black-body source.*

A light source emitting radiation, the spectral distribution of which is dependant on the temperature only and not on the material and nature of the source.

15. COLOUR TEMPERATURE.

The colour temperature of a light source is the temperature at which a full radiator would emit radiation of substantially the same spectral distribution in the visible region as the radiation from the light source and which would have the same colour.

The colour temperature of a light source which is a temperature radiator is of importance because it defines the colour-rendering properties of the light which it emits. The apparent colour of an object may be profoundly affected by the spectral composition of the light by which it is illuminated.

for example, certain colours which appear blue in daylight may, owing to a transmission band in the far red appear purple in light from an incandescent tungsten source, since in the latter the proportion of red light to blue light is much greater than it is in daylight.

With the development and widespread use of electric-discharge lamps, the determination of their colour-rendering properties has become of great importance. They are not temperature radiators, and in most cases have no equivalent colour temperature owing to the discontinuous nature of their radiation. Even the tubular fluorescent lamps now widely used in industry, although closely approaching standard temperature radiators or daylight in colour, are not sufficiently close in their spectral composition to be properly specified by their colour temperature. It has, however, become customary to specify the colour rendering properties of such illuminants by quoting the relative luminous flux in eight adjoining spectral bands (400–420, 420–440, 440–460, 460–510, 510–560, 560–610, 610–660, and 660–720 mμ). In U.S.A. nine spectral bands of different wavelength intervals have been adopted for the purpose, but the results are expressed in relative radiant energy.

16. LUMINOUS INTENSITY.

The property of a light source which determines the amount of light radiated per unit solid angle in any given direction.

17. CANDLE.

The unit of luminous intensity. Defined as the luminous intensity of an internationally agreed standard source.

18. LUMINOUS FLUX.

The amount of light being radiated.

19. LUMEN.

The unit of luminous flux. The flux emitted in unit solid angle by a uniform source having a luminous intensity of one candle.

C. SUBJECTIVE COLOUR TERMS.

It is difficult to describe sensations except in terms of the causal stimulus. Consider, for example, the difficulty of describing the sensation excited by dipping a finger into hot water. It is possible, however, to recognize equivalence and difference within certain groups of simultaneously or successively occurring sensations, by which means certain attributes of the sensations can be distinguished. They have to be defined subjectively and are not susceptible of direct measurement.

In addition to differences in spatial distribution and fluctuations with time, the eye appreciates three distinct ways in which the character of a visual sensation may vary, *i.e.*, it is possible to perceive three independent attributes of colour sensations. In Colour Physics these are hue, saturation, and luminosity, or in the case of secondary sources hue, saturation, and lightness.

20. HUE.

That attribute of certain visual sensations by which we distinguish red, green, blue, yellow, purple, etc., from one another and by which the eye distinguishes different parts of the spectrum.

This leads to the division of all visual colour sensations into two classes:

21. CHROMATIC COLOURS or CHROMATIC SENSATIONS.

Visual sensations possessing the attribute of hue. This is the sense of definition 2 (c).

22. ACHROMATIC COLOURS or ACHROMATIC SENSATIONS.

Visual sensations devoid of the attribute of hue.

23. *Brightness* (LUMINOSITY).

That attribute of visual sensations which permits achromatic sensations to be arranged in a series (obtained, for example, by varying the luminance of an extended source), and a chromatic sensation to be classed as equivalent to a member of such an achromatic series. Briefly, the intensity of luminous sensation.

Achromatic sensations differ in luminosity only. They fall into three classes:

24. WHITE.

An achromatic sensation of relatively high luminosity.

25. BLACK.

A visual sensation arising from some portion of a luminous field, of extremely low luminosity.

26. GREY.

An achromatic sensation of luminosity intermediate between black and white.

Chromatic sensations, in addition to differing in hue and luminosity, can also differ in a third attribute:

27. SATURATION.

That attribute of visual sensations which permits a judgment to be made of the proportion of colourfulness in the total sensation. Sensations of the same hue and luminosity can be arranged in a series of increasing saturation ranging from grey to that member of the series in which the hue appears most marked.

28. BLOOM.

The bloom (or "cast") of an oil is its colour by reflected light when this differs from its colour by transmitted light.

Bloom is associated with the power of the oil to absorb light of certain wavelengths and to re-emit the energy as radiations of longer wavelength. When the re-emission lasts only during the period of excitation, this phenomenon is known as fluorescence. When (as in the case of certain chemicals) the emission persists when the exciting source is removed, it is termed *Phosphorescence*.

Extended use of subjective colour terms.

The terms of this sub-section are, by an association of ideas, sometimes applied both to stimuli and to primary and secondary sources. Thus chromatic (achromatic) stimuli are stimuli which produce chromatic (achromatic) sensations. There is always an implied reference to the visual sensations, and the subjective implication of the terms should be recognized.

An additional concept is associated with the appearance of secondary sources:

29. LIGHTNESS.

That attribute of visual sensations by which one surface is judged to reflect a greater or smaller proportion of the incident light than another.

The sensation of lightness is not to be confused with the sensation of luminosity, since an object in shadow may have a higher lightness but a lower luminosity than an object more strongly illuminated.

Under the same conditions of observation, when direct comparisons can be made, lightness can replace luminosity as one of the three independent attributes of visual colour sensations arising from secondary sources. In fact, it is usual to consider hue, saturation, and lightness as the subjective colour attributes of secondary sources, and hue saturation and luminosity as the subjective colour attributes of primary sources.

D. COLORIMETRIC TERMS (OBJECTIVE).

The specification of a stimulus in colorimetry depends on the colour-matching properties of the eye. Two stimuli are of the same colour if the visual sensations they produce, under the same conditions of observation, match in every respect, *i.e.*, if the luminosity, hue, and saturation (sensations) are the same for each.

To effect a colour match it is necessary to adjust three independent quantities. The particular quantities employed depend on the method used to effect the match. In certain types of colorimeter three different stimuli (generally a red, a green, and a blue) are mixed additively. Provided the stimuli are chosen so that no one of them can be matched by a mixture of the other two, it is possible to match a large range of colours by varying the amounts of the three stimuli in the mixture, and all colours can be matched if in effect negative amounts of the stimuli can be used. This is accomplished in practice by mixing with the sample stimulus one or sometimes two of the three matching stimuli.

30. INSTRUMENTAL STIMULI, MATCHING STIMULI, *Primaries*.

The three defined stimuli of a trichromatic colorimeter.

31. STANDARD ILLUMINANT.

An agreed light source specified in such a way that its energy distribution is reproducible.

The units of the three matching stimuli are usually defined as the amounts contained in a mixture which matches some standard illuminant.

The Commission Internationale de l'Eclairage (C.I.E.) also known as the International Commission on Illumination (I.C.I.) established three standard illuminants designated by A, B, and C. Illuminant A is a gas-filled lamp operated at a colour temperature of 2848° K. Illuminants B and C are the same lamp used in combination with certain specified liquid filters to yield approximately colour temperatures of 4800° K. and 6500° K. respectively, corresponding to the yellower and bluer phases of daylight.

Any colour can be represented by a point in a space diagram obtained by plotting the amounts (positive or negative) of the three matching stimuli required for a match. Alternatively, the colour can be considered as a vector having three spatial co-ordinates.

32. TRICHROMATIC SYSTEM.

Any system of colour specification based on the possibility of matching all colours by the additive mixture (positive or negative) of three suitably chosen standard stimuli.

33. TRICHROMATIC CO-ORDINATES, TRISTIMULUS VALUES, TRISTIMULUS COEFFICIENTS.

The three co-ordinates of a colour in any three-dimensional trichromatic system of colour specification.

For the mixture of colours the simple laws of vector addition hold, the corresponding trichromatic co-ordinates of the colours being added. The specification of a colour in one trichromatic system can be transformed to another trichromatic system having different standard stimuli by means of the normal methods of mathematical transformation from one Cartesian system of co-ordinates to another. It is therefore not necessary that the standard stimuli of a trichromatic system of colour specification should correspond with the matching stimuli of a colorimeter.

34. ALYCHNE.

The locus in a trichromatic co-ordinate system of colours of zero luminance. It is a plane passing through the origin and lying wholly outside the boundary of realizable colours.

The C.I.E. trichromatic system of colour specification employs three imaginary reference stimuli denoted by X, Y, Z. The X and Z co-ordinate axes are chosen to lie in the plane of the alychne. They therefore have zero luminance so that the relative luminance of any stimulus is given directly by its Y co-ordinate. The XY plane of the system is made tangential to the red end of the spectrum locus (which approaches a plane in this region), and the YZ plane passes close to the spectrum locus, without touching, in a direction which gives a favourable disposition of the spectrum locus within the sector formed by the co-ordinate axes. The C.I.E. trichromatic co-ordinates u, v, w are therefore positive for all real stimuli including spectral colours. An equal energy stimulus is used for the basic stimulus.

35. DISTRIBUTION COEFFICIENTS.

The relative trichromatic co-ordinates of the spectral components of an equal energy spectrum. Denoted by $\bar{x}$, $\bar{y}$, $\bar{z}$, in the C.I.E. system and defined in a table of figures which represents the characteristics of the standard observer.

The function $\bar{y}$ corresponds to the relative spectral luminance function. In the tables of distribution coefficients officially defined by the C.I.E. the maximum value of $\bar{y}$ is arranged to equal unity. These tables are constructed from the results of accurate colour-matching experiments and embody the laws of colour matching. They enable the colour specification of any stimulus to be determined in terms of its trichromatic co-ordinates directly from its spectral energy distribution E_λ:

$$u = \int E_\lambda \bar{x}_\lambda d\lambda,\ v = \int E_\lambda \bar{y}_\lambda d\lambda,\ w = \int E_\lambda \bar{z}_\lambda d\lambda.$$

36. TRICHROMATIC COEFFICIENTS, CHROMATICITY CO-ORDINATES.

Three quantities, $u/(u + v + w)$, $v/(u + v + w)$ and $w/(u + v + w)$. Denoted by x, y, z in the C.I.E. system.

Since $x + y + z = 1$, only two of the three trichromatic coefficients of a colour are independent. They measure the colour of a stimulus independently of the luminance, since they define the direction only of the colour vector.

37. CHROMATICITY.

The colour quality of a stimulus, without reference to the luminance, as defined by two of the trichromatic coefficients (usually x and y).

The chromaticity can thus be represented by a point on a rectangular diagram obtained by plotting two of the trichromatic coefficients (usually x and y) against each other. Alternatively it can be plotted on an equilateral triangle known as the Maxwell triangle in which the perpendiculars to the sides from the point representing the chromaticity are proportional to the three trichromatic coefficients. The Maxwell triangle may be considered as representing the points of intersection of the colour vectors with the plane $u + v + w = 1$, and the rectangular chromaticity diagram as the parallel projection of the points on this plane on to the XY plane.

The colour vector of a stimulus in the C.I.E. trichromatic system is given by the vector equation

$$\mathrm{C} = u\mathrm{X} + v\mathrm{Y} + w\mathrm{Z}.$$

In America X, Y, Z are generally used to represent the trichromatic co-ordinates themselves, but the alternative term tristimulus values is used.

38. DOMINANT WAVELENGTH, *Hue wavelength, Dominant hue.*

The wavelength of the spectral stimulus required to be mixed (added or subtracted in the colorimetric sense) with a standard achromatic stimulus in order to match the observed stimulus. A negative sign is used in front of the wavelength if subtraction is necessary, *i.e.*, for purples.

39. PURITY.

(*a*) COLORIMETRIC PURITY.

The ratio B_d/B, where B is the luminance of the sample stimulus and B_d is the luminance of a spectral stimulus (or of a suitable combination of extreme spectral red and extreme spectral violet) which, by additive mixture with the adopted achromatic stimulus, forms a match with the sample stimulus in both luminance and chromaticity according to the data for the standard observer.

(*b*) EXCITATION PURITY.

The ratio of the distances, on a two-dimensional chromaticity diagram, from the adopted achromatic stimulus to the sample stimulus and to the stimulus lying on the spectrum locus or the straight line joining its extremes, which by additive mixture with the adopted achromatic stimulus can form a match with the sample stimulus.

An achromatic stimulus has purity $= 0$.
A chromatic stimulus has purity > 0 and $\neq 1$.
A spectral stimulus has purity $= 1$.

SUNBURY LUBRICATING OIL TEST ENGINE.

By J. R. Crowther, T. E. Pitkethly, and R. Stansfield (Fellow).

Summary.

Tests of lubricating oils have been made in many laboratories on many different engines during the last twenty years. As experience accumulated it became evident that the majority of commercial designs were rarely made with sufficient precision to enable repeatable results to be obtained either from duplicate engines or even from one engine for a long period of time.

It was concluded that a satisfactory design needed to be developed from the outset as an oil-test unit and that the use or conversion of existing commercial models was unsatisfactory. Test engines should be made of very heavy construction so that wear of all parts not connected with the test is reduced to a minimum, and special arrangements should be made for easy servicing, cleaning, and renewal of parts such as connecting-rod big-end bearings and cylinder liners.

A suitable engine should be capable of use as a replacement for the Chevrolet and Hercules units and possibly for preliminary grading prior to the Caterpillar test.

The design described has been run up to 4000 r.p.m. and can be modified for supercharge at 2400 r.p.m. if necessary. Either dry- or wet-sump lubrication can be used, and all auxiliaries are external to the engine. The crankcase is free from internal ledges, and slopes to give easy flow to the pump suction pipe. Main and big-end bearings may be either white metal or copper–lead. The crankshaft is hardened and ground, and arrangements are made for the use of a thermocouple to measure the temperature of the pin. Auxiliary drives are provided for magneto, fuel pump, or instruments, from two half-speed shafts and the crankshaft, and these project from the opposite end of the engine to the flywheel. The cylinder-liner thickness may be altered as required to control the cylinder-wall temperature, and the pistons may be either of cast iron or aluminium. Provision has been made for thermocouples in the piston crown and behind the top-ring groove. Either water or ethylene glycol can be used as the coolant for the cylinders, the head being cooled with water from a separate system. The oil temperature can be raised by means of an electric heater in the crankcase and cooled by passing it through a heat exchanger in the oil-pump circuit.

Introduction.

The testing of lubricating oils in engines has always been accompanied by considerable difficulties, especially in regard to reproducibility between one engine and another; these difficulties have been intensified when attempts have been made to duplicate results in different laboratories, and only during the last few years has it been possible to lay down the conditions for standardized tests and to obtain a limited number of engine types suitable for such work.

Much of the lack of real success with engine tests has been due to the use of commercially available engines rather than specially built units; in some cases failure to secure the required results arose from scaling down of size with consequent reduction of temperatures below those which it was desired to simulate.

Considerable oil-test experience has been obtained using the Caterpillar single-cylinder diesel engine, the Chevrolet six-cylinder automobile engine,

and the 6 G.M. 71 two-stroke high-speed diesel. These engines are among those used for approval tests for H.D. oils required to meet U.S. Army specification 2–104B.

As experience accumulated, it became clear that there was an urgent need for one or more special designs of oil-test engine which might be different in many respects from any prime mover of commercial importance but which would embody in their construction a number of features which had been found to control the significance and reliability of lubricating-oil engine tests. A decision was therefore made by the Anglo-Iranian Oil Co. Ltd. to prepare suitable designs and to manufacture a small number of prototype units for experimental purposes.

At a later date the Engine Tests of Lubricants Panel of the Institute of Petroleum Standardization Sub-Committee No. 5 agreed that a special engine was needed for tests of aviation lubricants and possibly as a substitute for the Chevrolet engine for bearing-corrosion tests. The Panel also recommended the design of a special diesel engine for testing H.D. oils.

The Sunbury design of petrol engine seemed to be applicable to the first part of these requirements, and it was reviewed in full detail by the Panel when suggestions, based on the experience of other laboratories, were incorporated. At the present time eleven of these engines are being built.

Special Requirements for Oil-test Engines.

An engine for testing lubricating oils must be designed so that the wear of all working parts not renewed between one run and the next is reduced to a minimum, and it should be possible to fit new parts without any machining operation being necessary. Simplicity of construction of the engine unit itself is important, as this provides for easy dismantling and assembly. As far as possible, auxiliary equipment should be mounted separately from the power unit so that only the latter needs to be removed from the test bed for inspection and overhaul between tests.

It is well known that the breakdown of engine lubricating oil may be caused by high temperatures in the crankcase, which lead to bearing corrosion and piston varnishing, by high cylinder-wall temperatures, which lead to heavy piston deposits and ring sticking, or by a combination of these causes. Some oils are also liable to give bad sludge deposits under low-temperature conditions. It is therefore necessary that any oil-test unit should be provided with means for running over wide temperature ranges for the crankcase oil and the cylinder-liner walls. If sufficient provision is made for proper temperature control there is evidence to show that a small petrol engine can give satisfactory ratings in respect of bearing corrosion, and at least serve for the preliminary sorting of detergent oils so that only selected blends of special merit need final tests in a diesel engine.

In a standard commercial design of engine, lubricating-oil temperature is determined mainly by the cylinder-jacket temperature, the running speed, and the mean pressure at which the engine operates. The liner-wall temperature also depends on the same factors. The range of possible wall temperatures may be increased by a suitable choice of coolants, but

only to a useful extent in the few designs where evaporative cooling with ethylene glycol is practicable. Recourse may also be had to supercharging, although this is rarely permissible with standard engines designed for normal aspiration. In the present unit steps have been taken not only to allow for the use of high-temperature cooling, supercharging, external oil heating, and a wide range of speed control, but provision has been made, in addition, for fitting cylinder-liners of various thicknesses or double liners with an enclosed stagnant air gap so that inner wall temperatures and the corresponding oil-film temperatures may be raised without difficulty to any required level.

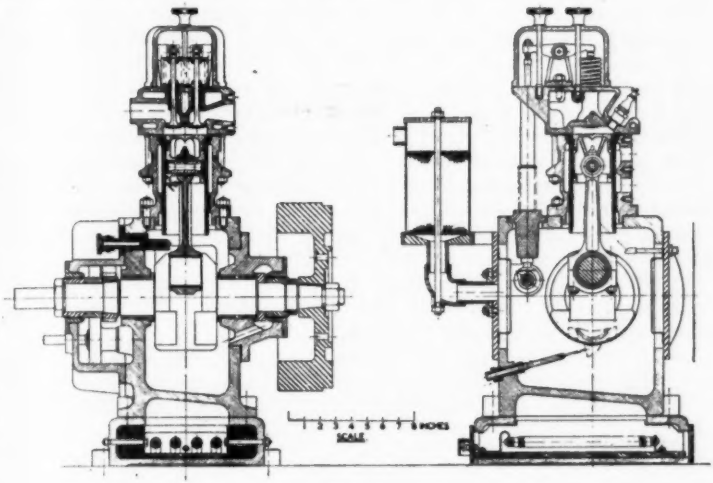


FIG. 1.

GENERAL DESCRIPTION OF ASSEMBLY.

The engine (Figs. 1 and 2) is a four-stroke design with a bore of $2\frac{1}{2}$ inches and a stroke of $3\frac{1}{4}$ inches. It has a detachable overhead-valve cylinder-head and a flat combustion chamber, and is intended to run normally aspirated at 100 p.s.i. b.m.e.p. and up to 3000 r.p.m. The scantlings are such that supercharged operation up to 300 p.s.i. b.m.e.p. at 2400 r.p.m. will be possible, although the higher outputs, if they are needed, are likely to require the design of an alternative cylinder-head with inclined valves and their associated more complicated valve-gear. The possible need for this modification has been borne in mind, and it can readily be applied when necessary.

The cylinder is a simple casting arranged to take a wet liner. The cast-iron crankcase is heavily built; the interior has been kept free from undesirable projections and ledges which make cleaning difficult, and its floor is sloped to give very easy drainage and good oil flow when dry-sump lubrication is used. The crankshaft is made of a nitriding-quality

steel (EN.40), hardened, ground, and super-finished on the bearing surfaces. Hardened-steel helical wheels are used for the timing gears, and an auxiliary shaft is driven from the camshaft at camshaft speed for use when both a magneto and a fuel-injection pump are required. Thus, there are three shafts, the crankshaft and two half-speed drives, projecting from the free end of the engine to operate auxiliaries, test instruments, etc., as necessary.

This simple unit can be removed, with its flywheel and carburettor, from the remainder of the assembly with a minimum of disturbance to other parts. The engine and the auxiliaries are mounted on a fabricated under-bed. This carries a radiant-type heater beneath the engine crankcase; a motor-driven lubricating-oil pressure pump, and, if required, a scavenge pump, an oil filter, an oil cooler, supports for a magneto and, if necessary, a fuel-injection pump or any similar equipment, and a framework to support the condensers for the cylinder-jacket and cylinder-head coolants. The cooling systems are separate so that the cylinder-head can always be cooled with water, even though the medium for the jacket may be ethylene glycol boiling at a much higher temperature.

The prototype engines will be run with carburettors modified to give control of mixture strength, and the power output will be absorbed by Heenan & Froude water brakes, type DPX1, although it is probable that a simple type of enclosed fan brake will be adequate for routine use when the test development is completed.

An oil-bath-type inlet-air cleaner is fitted to the carburettor, and provision is made for automatic control of the oil level in the crankcase and for the measurement of crankcase blow-by.

Each engine is used with a standard length of exhaust pipe, followed by a surge chamber which has a volume large enough to allow for considerable latitude in the exhaust arrangements beyond its outlet flange.

Lubricating-Oil System.

Fig. 3 is a diagrammatic arrangement of alternative methods of lubrication, which include a wet-sump system with pressure feed throughout, a splash-jet method for lubricating the connecting-rod big-end bearing, and a dry-sump system which may be required for testing aero-engine oils.

When the wet-sump systems are used, oil is drawn through a suction line from the lowest part of the crankcase to a motor-driven pressure pump which has a capacity of 300 g.p.h. From this pump it can be passed through a full-flow filter if required and then through a straight-tube cooler, valves being provided so that the cooler can be either entirely cut off or any required amount of oil by-passed for temperature control. The combined flow from the cooler outlet and the by-pass line is then fed to a large-diameter piston-type relief valve fitted with an adjustable and low-rate spring for pressure control, any surplus oil from the relief valve being returned direct to the engine sump. The outlet oil from the relief valve at a controlled pressure is then fed to several points in the engine itself. For full-pressure lubrication, a connection is taken to the timing-gear-end main bearing from which a supply is led through the drilled crankshaft to the connecting-rod big end and thence through the hollow rod to the small end. A branch pipe from the feed to the main bearing

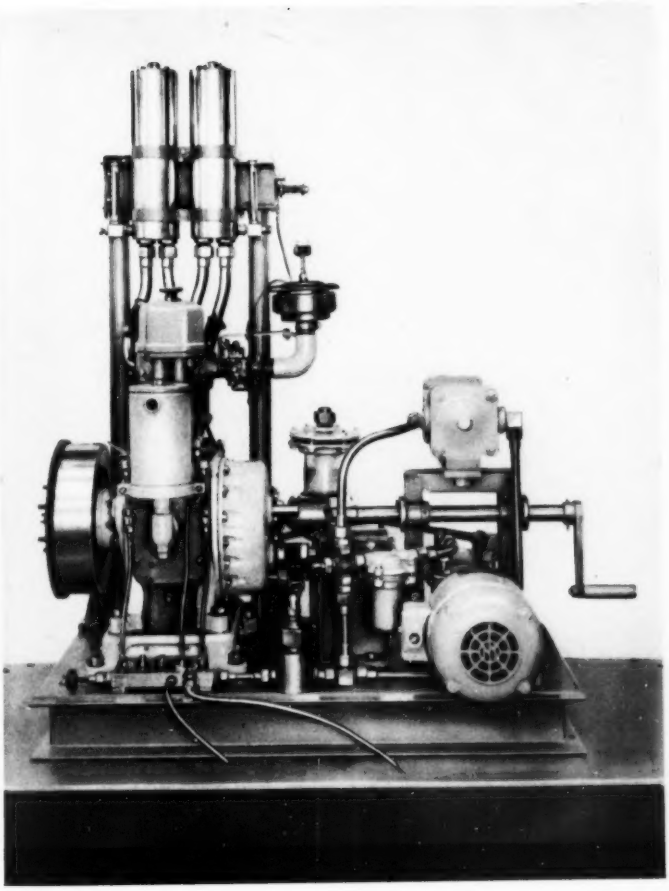
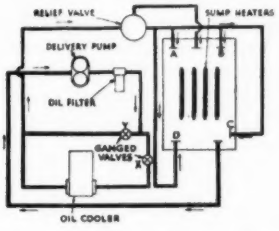


FIG. 2.

LUBRICATING OIL TEST-ENGINE ASSEMBLY.

[*To face p.* 248.

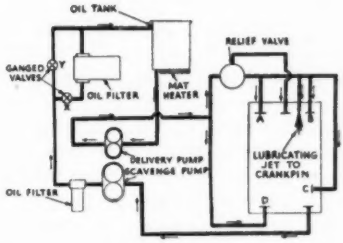
carries oil to two jets in the timing-gear casing, and these spray lubricant between the teeth of the two gear-trains. It is proposed to make use of these jets, which can readily be altered in size, to provide aeration of the oil. A separate feed pipe takes oil to the flywheel-end main bearing, and supplies are also arranged independently to each camshaft bearing and to the valve-rocker arms.



WET SUMP.

1. *Full heating.* Valve *X* closed, *Y* open, sump heaters on.
2. *Full cooling.* Valve *X* open, *Y* closed, sump heaters off.

Lubricating jet to crankpin is alternative to forced feed. Cooling jet to piston is optional in latter condition.



DRY SUMP.

1. *Full heating.* Valve *X* closed, *Y* open, heating mat on.
2. *Full cooling.* Valve *X* open, *Y* closed, heating mat off.

Lubricating jet to crankpin is alternative to forced feed. Cooling jet to piston is optional in latter condition.

FIG. 3.

LUBRICATION SYSTEM.

It has been claimed that one important factor determining the relatively good reproducibility of the Chevrolet engine bearing corrosion test is the use of a splash-jet feed instead of pressure lubrication to the connecting-rod big-end bearings. Arrangements have therefore been made for a suitable jet system of a similar type to be adopted as an alternative to the pressure supply if desired. It has also been commented that piston-ring sticking and lacquering may not only be determined by general engine conditions but also by the amount of oil splashed on the cylinder-walls from the big-end bearing. Since this quantity can alter considerably during the course of a few prolonged tests because of bearing wear, pro-

vision has been made so that a relatively large but controlled feed can be supplied from a jet to the cylinder-walls. With this arrangement normal variations due to change of bearing clearance should be unimportant.

Oil level is maintained constant in the wet-sump system by means of a chicken-feed control, coupled to the sump and mounted on a bracket near the engine. One of the crackcase doors carries an oil trap the outlet of which can be connected to a blow-by meter. The dry-sump system, which can be used as an alternative to the above arrangement, makes use of a scavenge pump and a pressure pump, both of which are driven from the same motor through flexible couplings. The scavenge pump has a capacity of 450 g.p.h. and draws oil from the engine sump, delivering it to an external oil reservoir fitted with a gauge glass and means for adding fresh oil when necessary. The crankcase breather pipe and the upper end of the oil reservoir are coupled together, and a branch taken from the connecting pipe to the blow-by meter. The pressure pump draws from the bottom of the oil reservoir and is connected on the delivery side to the engine through the filter, the cooler, and the relief valve already described.

All the lubricating-oil pipes are made of steel to avoid the catalytic effect of copper. If copper is to be included in the system it is preferred to introduce it in the form of a properly cleaned sheet of known area, either in the engine sump for wet-sump lubrication or in the oil reservoir when a dry-sump system is used.

Crankcase.

The general construction of the crankcase can be seen from Fig. 1. It consists of a heavy section box casting free from internal ledges which might collect sludge and be difficult to clean. The floor slopes to give easy flow to the oil-pump suction pipe.

The main bearings are steel bushes, which may be lined as required either with thin white metal or with copper–lead, the timing-gear end bush being pressed into the transverse wall of the crankcase. The wall at the flywheel end of the crankcase is bored to take a large dowelled end cover in which the flywheel-end main bearing is mounted. This bearing is in two halves, one being pressed in from each side with allowance for oil supply to an annulus between the bushes, which also take any thrust on their outer end faces.

This general construction makes a high degree of precision possible for bearing alignment and interchangeability. It does not allow for adjustment of bearing clearance in the manner possible with split bushes, but this is not considered desirable in an oil-test unit in which it is better practice to replace the crankshaft as well as the bearings once the former wears by an amount which leads to excessive clearance with standard bearings. Large crankcase doors are provided in line with the plane of rotation of the connecting-rod big end, and these are fitted with sheet-steel baffles, partly to ease the duty on the oil trap coupled to the blow-by meter, and partly to reduce unwanted cooling of the oil in circulation, much of which would otherwise splash directly against the doors themselves. A heavy cover is provided to enclose the timing gears and drain holes of liberal proportions are included to carry oil from both ends back to the

sump. The casting is drilled above the timing-gear-end main bearing for a retractable system of contacts for piston thermocouples. The upper surface of the crankcase is flat and machined to take the cylinder assembly and a block carrying the tappet rods. The first engines have been designed for vertically operating tappet rods, but enough space has been allowed for the use of an inclined valve gear should future developments lead to the use of supercharge and a pent-roof type of cylinder head. The camshaft bearings are pressed directly into the crankcase walls, that at the timing-gear end being a shell-type bush of large diameter, while the bearing at the opposite end consists of two smaller bushes pressed in from opposite sides of the casting and taking end thrust. The arrangement is such that withdrawal of the camshaft and cams can be effected without difficulty. Synthetic-rubber oil-seals are arranged where the timing-gear end of the camshaft and an auxiliary shaft project through the timing-gear cover. The ends of the crankshaft are sealed against oil leakage by means of piston-rings mounted in sleeves revolving with the shaft and fitting in highly finished bushes located in the timing-gear cover and the flywheel end cover respectively.

Crankshaft.

The crankshaft is made of nitriding-quality steel (EN.40) machined all over and fitted with balance weights bolted to the webs so that any necessary adjustment can be made to suit different pistons. The crankpin and main journals are nitrided, ground, and superfinished. The flywheel end of the shaft beyond the main bearing is reduced in diameter and fitted with a thrust collar and a sleeve carrying the blow-by sealing rings already referred to, these parts being held to place with a fine-thread nut. The flywheel fits on a taper beyond the thrust collar locking nut, and is located with a key and held to place with a fine-thread lock nut. Space is available around the thrust collar for an oil thrower, should this prove to be necessary, and alternative arrangements can readily be made for sealing against oil leakage and blow-by if desired. The free end of the crankshaft projects through the timing-gear cover so that it can be used either for hand starting or as an auxiliary drive, and it is fitted with a sleeve and blow-by-preventing piston-rings similar to those at the flywheel end. The sleeve is held to place with a fine-thread nut which also secures a distance collar and the taper bored and keyed pinion which drives the camshaft.

All the bearing surfaces are liberally dimensioned to reduce wear to a minimum. Lubricating oil is fed to the main bearing through a hole drilled in the crankcase and leading to an annular groove surrounding the bearing bush near the centre of its length, and the bush is drilled to conduct the oil to an annular groove inside. The crankshaft is drilled so that oil flows from this groove to the crankpin for lubrication of the big-end bearing and thence through the connecting-rod to the small-end; this part of the system can be plugged if splash lubrication from a jet is used. A second hole is drilled through the crankshaft from the flywheel end meeting a hole drilled diagonally in the crank web, which, in turn, meets a third hole drilled parallel to the axis of the crankpin and terminating close to the surface in the centre of the pin and at the top. This drilling is provided so that a thermocouple can be inserted in the crank-pin

journal for temperature control, the leads being taken to suitable slip rings built on the bobbin shaft normally used to couple the engine to a dynamometer.

Flywheel and Coupling.

The steel-disc-type flywheel is machined all over and can be fitted, if necessary, with a starter ring. Bolt holes are provided in the boss to take a flexible coupling or for the direct mounting of a fan brake. The rim of the wheel is graduated in degrees for timing purposes.

FIG. 4.

Timing Gears.

The timing gears are broad-faced single-helical wheels with a 10 deg. helix angle, the teeth being hardened and ground (Fig. 4). In addition to the main drive from the pinion on the crankshaft to the half-time wheel on the camshaft, a second pair of wheels can be fitted giving a one-to-one drive from the camshaft to an auxiliary shaft which may be used to operate a contact system such as that required in connexion with an engine indicator, or for any similar purpose. The auxiliary shaft would also be used if the engine were run with magneto or coil ignition and fuel injection from a fuel pump.

Camshaft.

The camshaft assembly consists of a spindle with a large central journal to suit the camshaft bearing at the driving-gear end. The shaft is reduced in one direction to carry the gears which are held to place with a fine-thread nut, and in the other, to take the cams. These are located endwise

by means of distance collars and keyed to prevent their rotation on the shaft (Fig. 4). The distance collar at the outer end is flanged to provide a thrust surface, and the various parts are held together with a fine-thread nut, which also acts as a thrust against movement of the shaft in the opposite direction. The shaft end is covered with a small oil-tight plate fitted on the outside of the crankcase end cover into which it projects. After dismantling the timing-gear end cover, the camshaft assembly can be withdrawn on removal of the oil-retaining plate and the fine-thread nut at the flywheel end of the engine. Oil for the camshaft bearings is led through holes drilled in the crankcase walls to an annular groove round the larger bearing and to the space between the two halves of the smaller one.

Cylinder and Liner.

One of the most important factors affecting the breakdown of lubricating oil in the piston-ring belt and on the piston skirt of an engine is the temperature of the cylinder wall. This is usually controlled in test engines by altering the coolant temperature, adjusting the running speed, and selecting a suitable b.m.e.p. Another variable, which can have a much greater effect than any small changes which are usually possible, is the design of the cylinder liner, especially at the upper end. This has always been designed in previous engines to suit the mechanical stresses imposed by the combustion pressures, and it follows that the smaller the engine the thinner has been the casting and therefore the cooler the inner surface for given running speeds and gas and coolant temperatures. In the engine under discussion loose liners are used so that they can be renewed from test to test if desired, and the cylinder-jacket is so constructed that, with a simple machining operation, different thicknesses of liner wall can be used without altering the cylinder bore or the piston. These liners are located in a register in the top of the cylinder, bedding on a well-machined inwardly projecting ring to which they may be lapped. They are made a light push fit in the lower part of the jacket casting, the coolant space being sealed with two rubber rings in specially shaped grooves. In addition, it is possible to fit two liners with a small clearance between them to approximate to air-cooled, sleeve-valve engine conditions. The coolant is supplied from an evaporative system of orthodox type and enters the jacket at the bottom. It circulates to the opposite side of the liner under the control of a deflector ring and then back to an outlet immediately above the inlet connexion. For development work, liners having a general thickness of 7/32 in and 5/16 in have been arranged for, the metal thicknessss of the upper flanges being 5/16 in and 7/46 in respectively.

Pistons.

Two designs of piston are available for preliminary tests, one being made of cast iron and having metal thicknesses in close agreement with the Chevrolet pistons used for the C.R.C. L-4 test. The other is a design in " Y " alloy. In both cases the gudgeon pin is mounted further below the piston-ring belt than is usual, this being done with the object of giving a reasonable area above the pin for lacquer accumulations and also to

reduce tilting of the piston during use. The pin is located endwise by means of circlips.

Arrangements have been made for fitting two thermocouples in the pistons when required, one, say, near the centre of the crown and the other in the wall immediately behind the top ring groove, to serve as temperature-control points. Thermocouple leads are taken down the inner wall of the piston to connexions attached to the inner rim of the skirt.

Connecting-rod.

The connecting-rod is made of EN.24 steel machined all over and fitted with precision-type bearing shells, those for the large end being available either with white-metal or copper–lead lining. The small-end bush is phosphor-bronze. The big end is lubricated as previously described. The rod is bored so that when the forced-lubrication system is used oil is carried to the small end. When desired this supply can also be used to feed a jet screwed into the top of the rod for piston cooling.

Cylinder-head.

The cylinder-head is of an unusual design, being secured to the cylinder block by means of long studs screwed into bosses in the lower face of the head and projecting downwards through a flange cast part way down the cylinder to take the nuts. This arrangement leaves the top of the head clear for valve springs, valve-rocker gear, and a valve-gear cover, and also considerably improves the water spaces. The combustion chamber is of the pancake type. The valves seat on inserts in the head casting, and the valve guides are renewable. The exhaust port is shaped to assist deflection of the gases away from the lower end of the exhaust-valve guide to give the best results when the engine is run on leaded fuels.

Piston Thermocouples.

Because of the importance of ring-belt and piston temperatures on the breakdown of lubricating oil, arrangements have been made in the design of the pistons and the crankcase to allow a thermocouple system to be fitted and this has already been examined in a high-speed engine to prove its reliability. Chromel–constantan thermocouples are used and are held behind the top-ring belt, in the piston crown, or elsewhere as required, the free ends being coupled to heavy spring contacts of the same materials fastened to an insulating block held to the lower rim of the piston skirt. The contacts project downwards and inwards towards the connecting-rod from this block at an angle of 45°. Reference has already been made to a hole in the crankcase wall above the timing-gear-end main bearing for use in connexion with piston-temperature measurements. A block of insulating material is fitted into this hole and projects so that its inner end almost touches the contacts on the piston when the latter is at the bottom of its stroke. Four contacts are screwed to a plate on the insulating block and project beyond a small platform on its inner end with a downward curvature so that they only just clear the piston contacts at the end of each downstroke. The block is bored to take a spring-loaded plunger, and a piece of insulating material is fastened to the inner end of

this so that its upper edge just touches the curved contacts, the lower face resting on a flat surface on the main insulating block on which it can slide. Leads are taken from the fixing screws holding the curved spring plates through small holes drilled in the insulating block to terminals on its outer face and thence to a temperature indicator of the potentiometer type. When temperature readings are required, pressure on the outer end of the spring-loaded plunger forces the inner sliding block against the undersurfaces of the curved contact springs and deflects them upwards sufficiently for the piston contacts to engage with a sliding motion at the end of each downstroke. This enables the required readings to be obtained. Care is taken to seal the leads coming through the block so that no crankcase gas leak can occur, and the plunger is fitted with a synthetic-rubber seal for the same purpose.

Constant-level Oil Feed.

Arrangements are made for keeping the oil level in the crankcase approximately constant when wet-sump lubrication is used. The feed system consists of a stout glass cylinder of about 1 litre capacity with sealed end flanges. The upper flange is fitted with a connexion for filling purposes, sealed with a conical plug and union nut. The lower flange is drilled centrally and a downward projecting pipe is brazed into it, the lower end of this pipe being recessed conically and sharp edged at the oil level which it is required to maintain. A second glass cylinder is located round this tube and is jointed between the lower flange of the main oil reservoir and another flange carrying a valve with a screwed stem which can be operated to shut off the oil flow by closing the conical end of the tube. The oil outlet to the crankcase is through a hole drilled in this flange, coupled by the necessary unions and pipe to the engine. A similar connexion is made through the upper flange of this part of the system to the gas space in the crankcase to provide a pressure balance. This arrangement gives a fairly close control of oil level, although small changes may take place due to temperature variations which lead to expansion or contraction of the air in the main feed vessel, with consequent minor surges or temporary stoppages of supply.

Blow-by Oil-Trap.

An oil-trap is fitted to one of the crankcase doors so that any blow-by gases escaping from the crankcase have to pass through a 5-in depth of glass packing beads before they are led through an outlet connexion to a blow-by meter.

Cooling-system Condensers.

Separate condensers are provided for the cylinder-jacket and the cylinder-head, so that the latter may always be cooled with water and the former with a coolant selected to have a boiling point giving the required jacket temperature. The connexions to the engine are of large diameter to give free circulation, and gauge glasses are provided to indicate the liquid level. The cooling coils in the upper part of the condensers are fitted in

an annular space round a central tube with a filling cap at the top of the tube. Two helically wound coils are used, the outer one being coupled to the inner one at the bottom with a cone-union connexion, while the inlet connexion to the inner tube and the outlet from the outer both project through the top flange of the condenser. This design simplifies the general construction and makes renewal of the cooling coils easy. A small valve is provided at the bottom of the gauge glass fitting so that excess coolant may be drawn off.

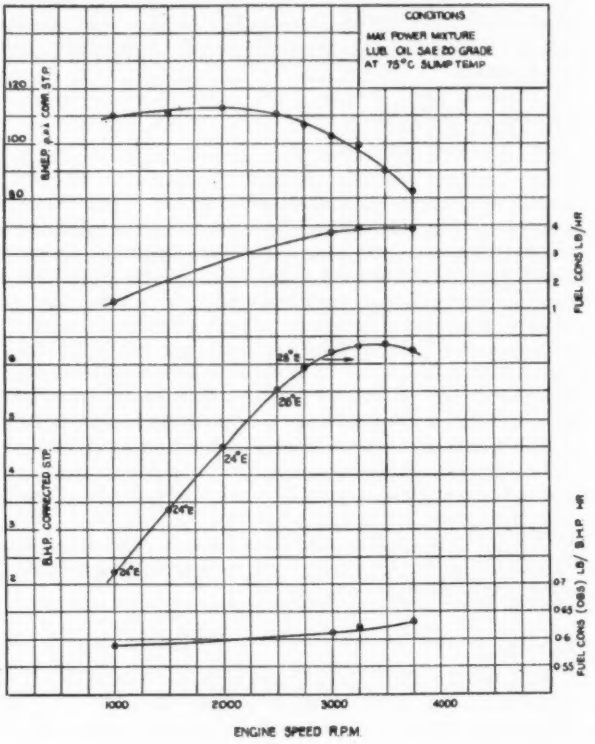


FIG. 5.

POWER AND FUEL CONSUMPTION CURVES.

Carburettor.

The carburettor is a Solex Type 26-AHD fitted with an adjustable jet to control air–fuel ratio. An A.C. oil-bath-type air-filter is fitted to the inlet, experience having shown that reproducible results in connexion with cylinder and piston-ring wear can be obtained only if the inlet air is thoroughly clean.

Magneto.

The magneto is a B.T.H. KD1 Form C6 T.T. replica and is mounted on a separate bracket external to the engine and driven through a rubber-sleeve coupling from the projecting end of the camshaft.

Starting.

Engines not coupled to electric dynamometers suitable for motoring may be started by hand cranking from a special handle fitted with pins engaging in a claw fitting on the end of the crankshaft, the shaft of the

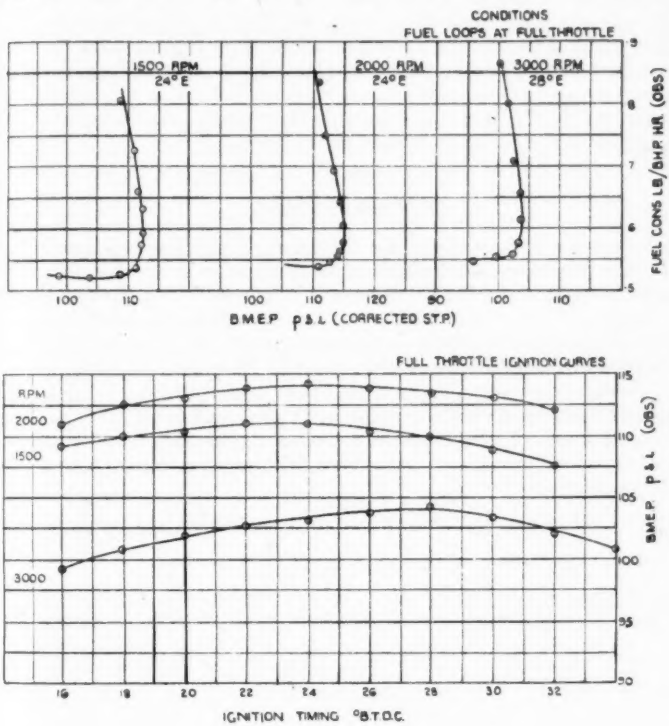


FIG. 6.

FUEL CONSUMPTION AND IGNITION TIMING CURVES.

handle being supported in the structure above the oil pumps. Alternatively a starter ring may be fitted to the flywheel for use in conjunction with a suitable battery-operated starter motor.

Performance Tests.

Details of test results from the first engine are given in Figs. 5 and 6. The maximum brake mean pressure, normally aspirated, is 113 p.s.i. at

about 2000 r.p.m. and the maximum power occurs at about 3300 r.p.m. when the b.m.e.p. is approximately 96 p.s.i. The design was intended to permit of normally aspirated running at 3000 r.p.m. and 100 b.m.e.p., and this has been obtained satisfactorily. The fuel consumption on full throttle varies from about 0·57 lb. per b.h.p.hr. to about 0·60 lb per b.h.p.hr. at the point of maximum horse-power. The compression ratio of the engine is 6 : 1, and in view of the very large bearing surfaces and the broad-faced timing wheels this performance is acceptable. Mixture loops are given in Fig. 6 for three speeds, and full-throttle ignition curves appear in the lower half of the same diagram. It will be noticed that the spark advance for maximum power is very little affected by speed.

The engine has already passed a 100-hr type test at 3000 r.p.m. and 100 p.s.i. b.m.e.p., and it is later intended to use it to determine whether conditions can be found which are suitable for rough sorting tests preliminary to the Chevrolet L-4 and the Caterpillar L-1 procedures, and to replace the R.G.2 aviation lubricating-oil test.

Acknowledgment.

The authors wish to thank the Chairman of the Anglo-Iranian Oil Co., Ltd., for permission to publish this description of the engine, and to acknowledge their indebtedness to the members of the Design Group of the Engine Tests of Lubricants Panel of the Institute of Petroleum for their criticism of the first design and their many useful suggestions, without which the development work would have been much more difficult and protracted. They also express their appreciation of the care and trouble taken by several manufacturers of component parts to provide details of unusually high precision under the conditions of considerable difficulty which are always connected with the making of new items in small quantities.

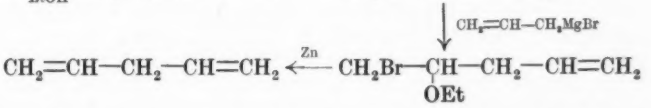
PENTA-1 : 4-DIENE.

By B. B. Elsner and E. R. Wallsgrove.

During the war it became necessary, in connexion with some problems on the composition of gasolines, to prepare a number of hydrocarbons of different types. The synthesis of one of these, penta-1 : 4-diene, was undertaken at the suggestion of the Anglo-Iranian Oil Company, and since the preparation involved a number of modifications of previously used procedures, the synthesis is described in this paper.

When this work was carried out in July and August 1942, there were only two unequivocal syntheses of penta-1 : 4-diene to be found in the literature. Krogerman [1] obtained the diene by the interaction of allyl bromide and vinyl bromide in ether solution in the presence of magnesium. The pentadiene obtained had to be purified by means of its solid tetrabromide and the yield was low—15 per cent on the vinyl bromide used. The interaction of allyl magnesium bromide and vinyl bromide gave no pentadiene : attempts to prepare vinyl magnesium bromide and to react this with allyl bromide were unsuccessful, as vinyl bromide did not react with magnesium in dry ether under the ordinary conditions.

In the same year, the Boord synthesis of olefins [2] was extended by Dykstra, Lewis, and Boord [3] to the preparation of penta-1 : 4-diene, by reacting αβ-dibromoethyl ethyl ether with allyl magnesium bromide and decomposing the resulting α-allyl-β-bromoethyl ethyl ether with zinc dust. This method was subsequently repeated and modified by Shoemaker and Boord [4] and by Kistiakowsky, Ruhoff, Smith, and Vaughan.[5]



This second method was the one used in the present work, with the principal modification that the readily available allyl chloride was used instead of allyl bromide.

Gilman and McGlumphy [6] determined the optimum conditions for preparing allyl magnesium bromide; using 3 g atoms of magnesium and 7·5 mols of ether to 0·5 mols of allyl bromide, they obtained the Grignard reagent in 90 per cent yield. Information in the literature concerning allyl magnesium chloride at the time of this present work was scanty. Houben, Boedler, and Fisher [7] made a survey of the yields in the preparation of organo-magnesium halides and, in small-scale runs, obtained a 16 per cent yield of allyl magnesium chloride, using ice-cooling and exclusion of air, with iodine as catalyst. By using ice–salt cooling they raised the yield to 19 per cent. Zoellner [8] reported that allyl magnesium chloride became colloidal and

was useless in 75 per cent of the preparations he tried, saying that this was one of the few cases where it was better to use the bromide rather than the chloride in preparing organo-magnesium halides.

In the present investigation, the first few attempted preparations of allyl magnesium chloride resulted in the deposition of a gelatinous solid, thought at first to be magnesium chloride etherate (by comparison with the results of Meisenheimer and Caspar [9] on allyl bromide). It was, however, found possible to obtain allyl magnesium chloride in 71 to 76·5 per cent yield, using *equivalent* amounts of magnesium and allyl chloride, by cooling the reaction mixture to −10° to −15° Centigrade in a freezing mixture of ice and salt or in alcohol and solid carbon dioxide and using bromine or iodine to start the reaction.

The allyl chloride had to be added slowly with careful control to avoid vigorous reaction and sudden heating up of the reaction mixture. In runs where such a rise in temperature occurred, deposition of solid followed immediately. Even in successful runs, deposition of a little solid sometimes occurred. It was thought that this might be due to traces of air or moisture, but even when using scrupulously dried ether, taking precautions against entry of moisture into the apparatus and working in an atmosphere of nitrogen, deposition of solid could not always be avoided.

A half-mol scale run was tried using benzene and a little ether as medium for the formation of allyl magnesium chloride, but even with the addition of bromine as catalyst, the reaction did not occur, either when cooled in a freezing mixture or when the ether was refluxed by warming on a water-bath.

A paper by Young, Andrews, and Cristol,[10] appearing after this work was completed, reported the preparation of allyl magnesium chloride by the method described by Young and Eisner [11] for butenyl magnesium chlorides. For this latter preparation, the optimum yield (86 per cent) was obtained using ether, magnesium, and the chloride in the molecular proportions 30 : 15 : 1; the proportions 19 : 10 : 1 were recommended for economy, though no details of the yield under these conditions were mentioned. Young, Andrews, and Cristol stated that the low solubility of allyl magnesium chloride in ether resulted in the production of a semi-solid mixture and reported an 84 per cent yield of Grignard reagent.

The overall yield of pentadiene from the four stages was 36 per cent, as compared with 19 per cent by Shoemaker and Boord,[4] and 37 per cent by Kistiakowsky *et al.*[5] 250 Cc of penta-1 : 4-diene of b.p. 26·1° to 26·15° at 760 mm, n_D^{20} 1·3886, n_D^{15} 1·3919, were obtained. Krogerman [1] gave b.p. 25·8° to 26·2° at 756 mm, n_D^{20} 1·3883, d_4^{20} 0·6594, tetrabromide, m.p. 85° to 86°; Shoemaker and Boord,[4] b.p. 28·5° to 29·2° at 742 mm, tetrabromide, m.p. 85·5° to 86·0°; Kistiakowsky *et al*,[5] b.p. 26·27° at 767 mm; while A.P.I. tables give b.p. 26·05° and n_D^{20} 1·388.

Between the completion of this work and the present time, several other preparations of penta-1 : 4-diene have been described and are listed here for completeness.

Paul and Normant [12] obtained penta-1 : 4-diene, b.p. 26·5° to 27·0° at 764 mm, n_D^{13} 1·3919, d_{16}^{13} 0·672, tetrabromide m.p. 85·5° to 86·0°, in 60 per cent yield by pyrolysis of pent-4-en-1-ol acetate over glass wool at 560°. Various methods of dehydrating pent-4-en-1-ol give either 2-methyl tetrahydrofuran or penta-1 : 3-diene or both, but no penta-1 : 4-diene.

Schniepp and Geller [13] pyrolysed pentan-1 : 5-diol diacetate at 575° in a stainless-steel tube, obtaining a 90 to 96 per cent yield of penta-1 : 4-diene, b.p. 26·8° to 27·4°, n_D^{26} 1·3865, d_4^{26} 0·675, tetrabromide m.p. 85·5° to 86·0°: they also found that the intermediate pyrolysis product, pent-4-en-1-ol acetate, yields penta-1 : 4-diene on similar pyrolysis. These observations are in general accordance with the observations of van Pelt and Wibaut,[14] who found that double-bond displacement or alteration of the carbon skeleton does not normally occur on pyrolysis of acetates, even where either or both of these occurs on dehydration of the corresponding alcohols. However, pentan-1 : 2-diol diacetate on pyrolysis under similar conditions gives penta-1 : 3-diene (Schniepp and Geller [13]), and Long [15] reported that pyrolytic decomposition of pent-1-en-4-ol acetate over glass wool at 550° to 570° under 70 to 80 mm pressure gave a 69 per cent yield of a mixture of penta-1 : 3- and 1 : 4-dienes.

Bateman and Koch [16] prepared penta-1 : 4-diene, b.p. 25·8°, by the Kistiakowsky modification of the Boord synthesis and measured the ultra-violet absorption spectrum.

Experimental.

α-*Chloroethyl ethyl ether.*

A mixture of 200 g of paraldehyde and 200 g of absolute ethanol (dried over calcium) was placed in a 2-litre three-necked flask, fitted with a mechanical stirrer, and cooled to about −5° in a freezing mixture. Hydrogen chloride was passed into the mixture until 200 g had been absorbed. The reaction mixture separated into two layers, the upper layer being the crude α-chloroethyl ethyl ether. This was separated off and a slow stream of air sucked through to remove much of the hydrogen chloride. The product was dried by allowing it to stand over calcium chloride. The reaction gave 414 g of crude material, corresponding to an 87 per cent yield based on the alcohol used. In all, about 1600 g of crude α-chloroethyl ethyl ether were prepared.

Kistiakowsky *et al* used a 3 : 1 mixture of alcohol and paraldehyde. This was found in the present work to give unsatisfactory results, the yield being as low as one-third of that by the above procedure.

200 G of the crude substance were distilled, yielding 159 g of water-white α-chloroethyl ethyl ether, b.p. 43° at 124 mm, some decomposition taking place. This corresponds to a 71 per cent yield of pure substance based on the ethanol taken.

αβ-*Dibromoethyl ethyl ether.*

200 G. of crude α-chloroethyl ethyl ether in a three-necked 1-litre flask, fitted with a dropping funnel, a stirrer, and a tube to lead off the hydrogen chloride evolved, were cooled in ice. 94 Cc. (294 g) of bromine were added in small portions with stirring, the solution being allowed to become practically colourless after each addition of bromine before more was run in. The product was pale yellow in colour and had pronounced lachrymatory power. A slow current of air was then passed through the solution to remove hydrogen chloride, and the solution was afterwards distilled under reduced pressure. The distillation gave 252 g of colourless product,

b.p. 76° to 78° at 30 mm. This corresponds to a 61 per cent yield of αβ-dibromoethyl ethyl ether based on the crude α-chloro-ether. Bromination of 159 g of pure α-chloro-ether (from 200 g crude) with 72 cc of bromine gave 147 cc (264 g ; *d* 1·7) of pure αβ-dibromoethyl ethyl ether, a 74 per cent yield. As there was some loss of α-chloro-ether by decomposition on distillation *in vacuo*, it did not seem worth while to purify the crude α-chloro-ether by distillation before bromination.

Dykstra, Lewis, and Boord recommended that the αβ-dibromoether be not distilled before proceeding to the coupling with the Grignard reagent, giving as the reason the loss in yield by decomposition on distillation. But as the crude product is liable to contain at least traces of hydrogen chloride, acetaldehyde, ethanol, and chloro-ether, all of which could interact with the Grignard reagent, purification by distillation was adopted. The product turned slightly yellow on standing, attacked rubber and cork, and had lachrymatory properties.

In all there were prepared 2096 g of αβ-dibromoethyl ethyl ether, b.p. 75° to 78° at 30 mm, n_D^{20} 1·5098.

α-Allyl-β-bromoethyl Ethyl Ether.

To 48 g of magnesium turnings and 1200 cc of ether in a 2-litre three-necked flask, fitted with an efficient sealed stirrer, reflux condenser, dropping funnel, and thermometer, was slowly added a solution of 163 cc of allyl chloride in an equal volume of ether. A few drops of bromine or a small crystal of iodine was added to start the reaction. The flask was cooled to between −10° and −15° in an ice–salt mixture or in solid carbon dioxide and alcohol. The rate of addition of allyl chloride needed careful control to prevent rise in temperature. It was found advisable to use at least 1200 cc of ether for a two mol run and to use the allyl magnesium chloride for the next stage as soon as it was prepared.

The amount of organo-magnesium halide in the ethereal solution (decanted or filtered from any solid to enable a representative sample to be withdrawn for estimation) was determined by acidimetric titration, using phenolphthalein as indicator—the method of Gilman, Wilkinson, Fishel, and Meyers,[17] as modified by Gilman, Zoellner, and Dickey.[18] Yields of Grignard reagent of 71 to 76·5 per cent were obtained.

10 per cent less than the equivalent amount of dibromoether in an equal volume of ether was run in slowly, the mixture being well stirred and cooled in ice-water. When the addition was complete, the mixture was allowed to stand overnight. 50 Cc. of 20 per cent acetic acid were then run in slowly with stirring, followed by 500 cc of water. The ether layer was separated, washed with water, sodium-bicarbonate solution, and water again, and dried over sodium sulphate.

After the ether had been distilled off on a water-bath, the residue was distilled under reduced pressure. Altogether, 943 g of α-allyl-β-bromoethyl ethyl ether, b.p. 75° to 78° at 24 to 26 mm, were obtained The refractive index of the different samples varied between 1·4589 and 1·4596, mean 1·4591. The yield in six runs varied between 72 and 76 per cent.

Some of the ether recovered from the reaction was distilled through a column to see if any diallyl (hexa-1 : 5-diene), b.p. 59°, was present, but no trace of it was to be found.

Penta-1 : 4-diene.

521 G. of α-allyl-β-bromoethyl ethyl ether were dissolved in 680 cc of *n*-butanol in a 3-litre three-necked flask (fitted with a sealed stirrer and a short reflux condenser, above which was mounted a fractionating column) and 680 g of zinc dust added, followed by 3 g of zinc chloride. The whole was vigorously stirred and heated gradually. The short reflux condenser kept back the butanol, the pentadiene passing through the column and then through a condenser set for downward distillation, being then condensed an ice-cooled receiver, attached to a trap cooled in solid carbon dioxide and alcohol. The rate of heating and the rate of flow of water through the reflux condenser was adjusted so that the diene distilled over at the rate of about one drop every 2 sec. The reaction took 5 to 6 hr for completion.

A second batch of 422 g of α-allyl-β-bromoethyl ethyl ether was similarly treated with zinc dust.

The combined products were washed six times with ice-water to remove traces of butanol and then dried over calcium chloride, giving 295 g of pentadiene (89 per cent on α-allyl-β-bromoethyl ethyl ether). This was carefully fractionated through a column (three 30-cm Dufton spirals), giving a main fraction (*ca* 250 cc) of b.p. 26·1° to 26·15° at 760 mm, n_D^{20} 1·3886, n_D^{15} 1·3919. The pentadiene reacted with concentrated sulphuric acid, going rapidly to a gum; it was stable to sodium.

Acknowledgments.

The authors wish to thank Dr J. C. Smith for his interest in this research and for his helpful advice. One of us (E. R. W.) also expresses his gratitude to the Department of Scientific and Industrial Research for a grant.

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THE INFLUENCE OF TETRA-ETHYL LEAD ON ENGINE DESIGN AND PERFORMANCE.*

By F. R. Banks, C.B., O.B.E. (Fellow).

Introduction.

History, if it is accurate, is always worth while and serves as a reminder that those who came before us were not so stupid as the younger generation are often apt to think. In fact, the brilliance and original thought shown by some of the early research workers on the internal-combustion engine could shame many who accept much of their pioneer work as normal and commonplace.

There has certainly been much advance since the early days, but a good deal of the progress has, unfortunately, been as the result of two major wars. The early workers had no such incentive. It is also true that our knowledge of fuel has progressed, and that better engines can be made to use it. But can anyone yet explain the actual chemical mechanism of detonation?

The story of tetra-ethyl lead is really the story of the efforts to suppress detonation in the gasoline engine. However, before going into the history of tetra-ethyl lead, it should be placed on record that the first man to distinguish the difference between detonation and pre-ignition, and who identified detonation as a characteristic of the fuel itself, was the late Professor Hopkinson, when he was working at Cambridge University in the early 1900s. It was Hopkinson who found that the dull thudding of pre-ignition in the engine cylinder was quite different from the sharp metallic knock of detonation.

According to Ricardo,[1] who worked with him in his (Ricardo's) undergraduate days, Hopkinson did not believe that the metallic or ringing knock in the cylinder was due to pre-ignition and considered that it could be accounted for as gas shock. He, Hopkinson, said that there was insufficient heat energy in the working fluid to produce the high pressures which he had traced on the indicator of his own design. To prove his theory, Hopkinson fitted a long steel bolt which projected well into the combustion chamber of the cylinder of a gas-engine. This bolt quickly reached a temperature which caused pre-ignition to occur and, by watching Hopkinson's indicator, it was possible to see "the gradual transition from normal to premature ignition, which advanced as the bolt heated up until it (ignition) became so early as gradually to pull the engine up altogether." Further study of this process by Hopkinson and Ricardo disclosed three interesting points:—

First: That genuine pre-ignition was accompanied by a dull thud, and there was no trace of the ringing knock found in the petrol engine.

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* An address delivered on February 22, 1949, to the London Branch, Institute of Petroleum.

Second: That the maximum (pre-ignition) pressure never, under any circumstances, exceeded the normal maximum. [This does not necessarily appear to hold good in the case of the modern high-duty (aviation) engine, where peak pressures some 40 per cent higher than normal have been recorded.]

Third: That the rate of pressure rise, during pre-ignition, as recorded by the indicator, was no more rapid than the pressure rise rate of normal combustion.

This work confirmed Hopkinson's belief that the knock in the petrol-engine cylinder was something quite distinct from pre-ignition, and he, in fact, described it as in the nature of a detonating explosion.

He must have been the first man to evolve the "physical" explanation for detonation which was due, in his opinion, to the shock of a gaseous wave striking the walls of the cylinder, and he attributed this to some peculiarity of the fuel.

All this happened in 1905, and Ricardo placed it on record in his paper referred to above. In the same paper, Ricardo records that Hopkinson called his attention to the very great difference in the rate of burning of the same working fluid in an engine cylinder compared with its combustion in an explosion vessel. Explosions in "bombs" had shown that the normal rate of burning was so slow that it would be less than half-completed by the end of the working stroke, even in quite a slow-speed engine. As Ricardo puts it, "*this glaring inconsistency had been overlooked by previous observers, though Sir Dugald Clerk was at the time puzzled by it. Hopkinson explained it by arguing that the rapid spread of burning in the engine cylinder was due to the rapidity of movement of the gases—in fact, to turbulence.*" The actual term "turbulence" was used much later to describe the agitation or vigorous movement of the gases.

In order to test his theory, Hopkinson fitted an electrically driven fan inside an explosion vessel and, by speeding up the fan, he was able to obtain a rate of burning as rapid as that in an engine cylinder. Some years after this experiment, Clerk carried out his classic experiment which was, essentially, the reverse of Hopkinson's. He (Clerk) produced stagnation of the working fluid in the engine cylinder by letting the engine run for several idle cycles and then switching on the ignition. The turbulence had been so reduced by this means that the rate of burning was slowed down to the point where combustion was less than half-completed by the end of the working (expansion) stroke.

Ricardo has since followed well in Hopkinson's and Clerk's footsteps, and his basic work on fuel behaviour in the internal-combustion engine, and the behaviour of the engine itself is universally acknowledged and need not be described here.

American Anti-detonant Research.

The scene now shifts to the first world war, when work on detonation and anti-detonants was initiated in America (1916) by Charles F. Kettering at the General Motors Research Corporation laboratory in Moraine City, Ohio. Kettering's team was headed by Midgley, who was

directly responsible for this research, and included T. A. Boyd, Carol H. Hochwalt, and James P. Andrew.

Kettering and Midgley were convinced that detonation, or engine knock, was due to the (chemical) characteristic of the fuel. Midgley had tried such fuels as benzol and *cyclo*hexane, which he found were much more resistant to detonation than gasoline. He also discovered that gasoline was, in turn, much superior to kerosine in respect of detonation.

Midgley's extraordinarily active brain was continually evolving theories to explain the phenomenon of detonation, and these theories were successively discarded as further experimental work refuted them. One of the earliest of his theories was the result of an attempt to understand why kerosine detonated more readily and more heavily than gasoline in an engine. He thought that the difference in volatility might explain this, where some of the kerosine persisted in droplet form after combustion had commenced; these droplets then vaporized very suddenly, thus causing a detonating type of explosion. He reasoned, if this explanation were correct, that by adding dye to the kerosine it might be possible to make the droplets absorb radiant heat and thus vaporize very early in the combustion process.

He tried iodine in the kerosine and found that the detonation disappeared! As the natural consequence a number of oil-soluble dyes were tested, without any success. He then returned to iodine, which he added in the form of a colourless compound, ethyl iodide. Ethyl iodide stopped knock, and this fact finally satisfied Midgley that his colour theory, as it might affect combustion radiation, was unsound. But he was more convinced than ever that detonation was a chemical problem to do with the fuel itself and must be attacked as such.

Midgley was a mechanical engineer by training and had little real knowledge of physics or chemistry, but in the early 1920s he decided to study chemistry in all its branches in order to give himself a better understanding of the chemical aspects of his work.

Then came into the picture a Dr Robert Wilson, who had returned from the U.S. Chemical Warfare Service and had been appointed Director of the Research Laboratory of Applied Chemistry at the Massachusetts Institute of Technology. He and Midgley got to know each other very well and, by frequent contact and the exchanging of ideas, much valuable work resulted. In the autumn of 1920, Wilson was asked to serve on the Advisory Committee of the American Petroleum Institute. The Committee was formed in order to recommend research problems which the Institute might finance. It was at the first meeting of this Committee that Wilson discussed with Midgley the latter's work on anti-knock agents.

Midgley was at that time enthusiastic of the possibilities of aniline, although he still had hopes for his first compound, ethyl iodide. Apparently Midgley, in his practical way, always considered the eventual commercial application of his discoveries and would go to considerable lengths to ascertain whether or not the particular compound could be manufactured in quantity and at reasonable cost.

Later, Midgley found that diethyl telluride was much more effective than any of his previous compounds, but diethyl telluride had one bad

drawback in that, when minute quantities were inhaled or absorbed through the skin, there resulted unpleasant symptoms such as a "*strong garlic-like odour given off from every pore of the body and affecting everything and everyone with whom the victim came in close contact.*"

This did not deter Midgley, who said that just so soon as the entire population got "infected" the problem would disappear, since the victims would soon be unable to detect the odour! Wilson has stated that we may be grateful for the discovery of tetra-ethyl lead because, if it had not been found, Midgley would undoubtedly have tried to develop the use of diethyl telluride as a commercial anti-knock agent for motor fuel.

Later, Wilson showed Midgley a new chart of the periodic system which he had drawn up and where he had arranged the elements according to both their electro-positive and electro-negative properties, in accordance with Langmuir's octet theory, and bringing out certain relationships which had not previously been appreciated. It was from this chart that Midgley found that the anti-knock properties of various agents could be related primarily to the properties of the elements, and there were indications that the anti-knock value of an element could be predicted to vary with its location in the periodic system.

It was Wilson's rearranged chart of the periodic system which was largely responsible for Midgley trying the various organic metallic compounds. He also built a scale model of the periodic table and used pegs to show the results of experiments already made and to indicate the probable effectiveness of other compounds. The compounds which gave indifferent or unsuccessful results were indicated by short pegs, and the more promising compounds which had already given some results, or were theoretically interesting, were marked by longer pegs. The evidence, "tabulated" in this manner, showed Midgley, graphically, that derivatives of the ordinary and familiar metals held the most promise.

He and his co-workers then investigated the anti-knock properties of tin tetrachloride, and followed this by trying its ethyl derivative. Tetra-ethyl tin was found to be much more potent as an anti-knock agent than they had suspected. It was after the results of this particular series of tests that Midgley decided to try compounds of the heavier or higher density metals and eventually hit upon tetra-ethyl lead, which at that time was purely a chemical curiosity and had then been made in only very small (laboratory) amounts.

Tetra-ethyl lead was first tried practically, in a single-cylinder Delco engine, in December 1921. It proved to be completely outstanding as an anti-knock specific, or agent, and was far superior, in terms of effectiveness for the (minute) quantity used, to any of the other compounds tried.

Lead Scavengers.

It was soon found that tetra-ethyl lead, when used by itself, quickly built up deposits of lead oxide in the combustion chamber, causing fouling of the sparking-plug after only a few hours' operation. This was a set-back, and considerable experimentation was involved in trying to find a chemical compound which would combine with the tetra-ethyl lead during the combustion process and act as a scavenger or evacuant.

Eventually, Midgley found a halogen bearer in the form of a bromine compound, ethylene dibromide, which was miscible with tetra-ethyl lead and also with gasoline. Ethylene dibromide combines with the lead during combustion to form lead–bromine compounds, which are volatile at the conditions in the engine cylinder and are eventually evacuated during the exhaust stroke. Since, like other chemical reactions, this process in the engine cylinder is not perfectly completed, some products remain in the form of deposits. This, of course, is also true of the fuel itself where free carbon remains after combustion.

When ethylene dibromide was first used, it was added to tetra-ethyl lead in the quantity equivalent to 1·5 theories, or more than the theoretical amount (by 0·5 theory) required to combine completely with the whole of the lead present. Later, the quantity of bromine was reduced to one theory, at which value it has since remained for the particular fluid mix used for addition to aviation fuel. This fluid is known as " 1-T. Aviation Mix." For motor-vehicle gasoline, a mixture of ethylene dibromide and ethylene dichloride to the equivalent of 1·5 theories is used, *i.e.*, 0·5 theory ethylene dibromide and 1·0 theory ethylene dichloride. The fluid is known as " Motor Mix."

" Ethyl " anti-knock compound was first sold to the public on February 2, 1923, from a single service station in Dayton, Ohio. For the sake of brevity, " Ethyl " anti-knock compound will be referred to in this paper as " Ethyl " or " Ethyl fluid " and will be taken to mean a mixture of tetra-ethyl lead with halogen bearers or scavengers.

" Ethyl " fluid was first made up and packaged in cans of 1-litre capacity, from which it was added to bulk quantities of gasoline. Then came the 55-U.S.G. drum, which was used for shipping lead to the refineries and blending points. Now, bulk quantities of " Ethyl " are transported and delivered in 40-ton rail tank-wagons, within the North American Continent—U.S.A. and Canada; and similar methods will be used for the transport of fluid in bulk in those countries, such as Great Britain and France, which also have tetra-ethyl-lead-manufacturing plants. But the 55-gal drum still remains the standard container for overseas shipments.

There were many difficulties to solve after the discovery of tetra-ethyl lead as an anti-knock agent. Not the least of these was concerned with its manufacture in bulk, at a price which would make it worth while to the oil refiner. Then came the question of obtaining sufficient bromine.

It was thought that bromine might be obtained from seawater, but since there is only a minute quantity of bromine in seawater, *i.e.*, about 67 parts in every one million parts of seawater, it seemed at first that the difficulties of obtaining sufficient bromine would be very formidable. However, a semi-experimental pilot plant was set up at Ocean City, Maryland, in the winter of 1924–25. The results from this plant indicated that the separation of bromine from seawater was a practical possibility.

The bromine extraction theory was further tested when a former Great Lakes steamer, renamed S.S. *Ethyl*, was converted into a floating factory and cruised in the waters of the Gulf Stream for a week in April 1925. The results of this experiment proved that bromine could be recovered from seawater on a commercial basis; even although the extraction plant on board only operated for a total of about 6 hr, at the cost of some

$60,000 an hour, mainly because all the chemist personnel on board were violently sea-sick! The total cost was, therefore, somewhere around $360,000 (£90,000), but was worth the expense, effort, and physical discomfort.

At the present time, the practical results of these early experiments are evident in the form of two Ethyl-Dow bromine-extraction plants at Kure Beach, North Carolina, and at Freeport, Texas. The former installation has not been in operation since the recent war, but is used as a standby for the Freeport plant. The latter is capable of a yearly production of 30 million lb of ethylene dibromide.

The Associated Ethyl Company of Great Britain has a bromine-extraction plant in Cornwall, in order to supply its lead plant at Northwich, Cheshire, and a similar plant is operated by the affiliated company in France.

Toxicity and Sales Resistance.

It is well known that tetra-ethyl lead is exceedingly toxic in its concentrated form and can also be absorbed into the human system by inhalation and through the skin. It is, however, quite safe to handle and is innocuous to the ordinary road user when diluted in gasoline in the commercial proportions. Full medical precautions are naturally taken during the manufacture of tetra-ethyl lead and when blending it with gasoline.

But the first sales of " Ethyl " gasoline to the public in America and, in 1928, to the public in Great Britain were not untroubled. In fact, there was considerable opposition in the States when the Press got word of an accident which occurred in the first experimental manufacturing plant, where an autoclave burst and, unfortunately, caused the deaths of some of the staff. The Press did not discriminate between an accident in a semi-works or experimental plant, which was being used to develop the manufacturing process, and the use of the same product in minute quantities in gasoline.

Resulting from this, an investigation was started by the Surgeon General of the U.S. Public Health Service to find out whether or not the public health would be endangered by the use of " Ethyl " gasoline. Pending the results of this investigation the Board of the Ethyl Gasoline Corporation decided to suspend the sales of " Ethyl " gasoline and withdrew it from the market on May 5, 1925.

As the result of an exhaustive investigation, the Surgeon General decided, in January 1926, that there were " no good grounds " for prohibiting the use of " Ethyl " anti-knock compound in gasoline, provided that proper safety regulations were observed; and " Ethyl " gasoline was put back on the market again in the summer of 1926. The sales area then consisted of twenty-eight States, but it was later obtainable in every State in the Union.

In Great Britain in 1928, almost as soon as " Ethyl " petrol was put on the market, and certainly when the automobiles using it could have been numbered only in the hundreds, its sale was brought down to a negligible amount due to an uninformed and irresponsible Press campaign, in which were also involved men of scientific and technical attainment. This campaign eventually led to the holding of a Government enquiry, as the

result of which the product was vindicated from the health point of view. But these attacks certainly delayed the general acceptance of tetra-ethyl lead as an anti-knock specific in Great Britain, and the effects were also felt in other countries for some years afterwards.

However, the almost universal use of lead to-day, both in motor and in aviation fuel, is proof that persistence does pay in the end—but with the proviso that the product must be basically sound in the first place. In the particular case of tetra-ethyl lead, this faith in its potential value to the petroleum and motor industries was coupled with considerable care and foresight to ensure that it was manufactured and handled properly, and always under strict medical control and supervision. In addition, there has continued to be ceaseless research and development to improve the engine condition, when leaded fuel is used, and to find a still better anti-knock compound, if possible. So far, no such effective alternative has been found.

Early Efforts to Standardize Laboratory Knock-testing Procedure.

After the Ethyl Gasoline Corporation (now Ethyl Corporation) was formed in America, to manufacture, develop, and market "Ethyl" anti-knock compound, and to supply it to the oil companies, Midgley continued to act as a consultant to the Corporation while, at the same time, he worked on other projects for General Motors Corporation. He had, in his anti-knock researches, developed the original "Delco" fuel-knock-testing engine and the bouncing-pin method of measuring knock, later to be followed and superseded by the CFR engine. It was he who also developed the fluorine compounds as safe refrigerants. In fact, Midgley, from starting as a mechanical engineer, became one of the leading chemists of America.

The next development in the field of fuel detonation came as the result of a natural and logical desire to be able to rate or measure the detonation resistance of a fuel, and to compare one fuel with another. It was from the brain of Dr Graham Edgar, who was then in charge of the chemical research of the Ethyl Gasoline Corporation, that the octane scale was evolved. The octane scale was generally adopted in 1930, and it represented a great step forward in the detonation evaluation of a fuel, even although it could be regarded only as a yardstick of measurement. But it was a more stable yardstick than others which had been used previously.

Up to that time, the various fuel-test laboratories used the ingenious "highest useful compression ratio" (H.U.C.R.) method of Ricardo and, also, the "benzol equivalent" and "toluene-number" methods of evaluation. For those interested, these are fully described in the Report of the Empire Motor Fuels Committee.*

Practical Application of "Ethyl" Anti-knock Compound.

One of the first endeavours of the sponsors of "Ethyl" was to get experience of the product under practical conditions in road service.

* Institution of Petroleum Technologists, London, 1924.

Therefore, they sought the co-operation of The Dayton Power & Light Company, which had a large fleet of cars on the road. These cars were run on leaded gasoline from 1923 onwards and were kept running on leaded gasoline during the year it was withdrawn from general sale, in order to provide further clinical information for the Surgeon General in connexion with his investigation.

The Company has continued to use leaded gasoline ever since and has always proved a very willing and valuable "control" for the Ethyl Corporation in its further investigations.

The first and, so far as the author is aware, the only engine specifically adapted to use leaded gasoline of (then) high anti-knock value was the Chrysler "Red Head," which was introduced as a new engine and was made available optionally to the customer, to take the place of the standard engine in the same chassis. It had a high-compression cylinder-head which was painted red, and "Ethyl" gasoline was specified as the fuel to be used.

It might be asked why the "Red Head" did not start a trend of American engines specifically designed to use leaded fuel or, at any rate, to use high anti-knock fuels, particularly since leaded fuel was in general distribution in the States from 1926 onwards. A direct answer to this question is difficult to find, but there is, in the author's opinion, one reason why this did not come about. It relates to the very high rate of automobile production in the States, which was then building up to an enormous peak, and consequently the reluctance of the American automobile manufacturer to make radical alterations which would mean the scrapping of millions of dollars' worth of tooling. But he later appreciated the advantage of using high anti-knock fuels and, in the 1930s, there were a number of American automobile manufacturers who offered a high-compression cylinder-head as an alternative to the standard head.

It is now interesting to record that, whereas the production of tetra-ethyl lead in 1923 amounted to only a few hundred 1-litre cans, its present production is in excess of 130,000 tons per annum; and plans are already in being to increase production capacity by at least another 40,000 tons per annum.

In Table I are given the constituents of the two types of "Ethyl" anti-knock compound at present in use, together with some physical data.

It will be noted that "Motor Mix" contains ethylene dichloride, in the larger proportion, as a halogen bearer and lead scavenger. The reason for this is that dichloride was, earlier, in better commercial availability than bromine and, therefore, to conserve the latter, it was decided to use some dichloride in "Motor Mix" rather than risk modifying "Aviation Mix," which was becoming established in aviation fuel and had already some operational background.

No particular disadvantages or troubles were experienced with ethylene dichloride in "Motor Mix" fluid. Its vapour pressure, which is higher than that of ethylene dibromide, was at one time considered to be of some advantage when used with the latter in an engine having varying load characteristics, such as the typical automobile motor. This theory has not been proved, one way or the other, although ethylene dichloride continues to be used satisfactorily. In any case, no alternative could be

considered without first obtaining mass data from the results of careful and thorough tests, which would take a year or more to complete, before a new scavenger could safely be accepted. And no alternative of sufficient promise has yet presented itself.

TABLE I.

Physical characteristics.	Designation.	
	Aviation mix.	Motor mix.
Sp. gr.	1·744	1·592
T.E.L. content, cc/lb fluid	168·83	169·01
Ratio of fluid/T.E.L. by volume	1·5405	1·6858
Flash point, ° C	Above 110°	Above 110
Freezing point, ° C	−9	−33
Theories of halogen	1·0 Br	0·5 Br 1·0 Cl
COMPOSITION:	Per cent.	Per cent.
T.E.L. (100 per cent)	61·41	61·48
Ethylene dibromide	35·68	17·86
Ethylene dichloride	Nil	18·81
Dye	0·05	0·12
Kerosine and impurities	2·86	1·73
	100·00	100·00

The amount of tetra-ethyl lead, and not " Ethyl " anti-knock compound, is given when referring to concentrations in the fuel, since it is the lead which is the active anti-knock agent. The maximum concentration of lead which is allowed in motor gasoline, for commercial use, is 3·6 cc per Imperial gallon (4545 cc) or 0·8 cc per litre (1000 cc). The maximum concentration in aviation fuel is 5·5 cc per I.G., or 1·21 cc per litre. This maximum may, however, be raised to 7·2 cc per I.G., or 1·6 cc per litre, for the aeronautical branches of the Government, when so required.

To avoid confusion, there are two separate points to consider where lead is concerned. First, there is its primary use to improve the anti-knock value of the fuel and, second, there is its effect upon the engine.

AMERICAN AND BRITISH AUTOMOBILE PRACTICE.

Before discussing the more technical aspects of tetra-ethyl lead and its influence upon the fuel and the engine, some brief information on the characteristic differences in American and British outlook and technique in regard to the automobile or motor car will be given.

It is not often appreciated that until the last year or so, when some new engines were produced, the basic engine design of the average American car was between fifteen and twenty years old. Some British engines are almost as old in their conception, although in Great Britain, until recently, the automobile has largely been regarded through the eyes of an enthusiast who is interested in a piece of mechanism and, therefore, more frequent changes of engine design have been accepted. In contrast, the American

regards the automobile entirely from a utilitarian angle as a means of personal transport. The result of taxation, relatively poor motoring roads, and the enthusiastic type of owner have all had their influence upon British car design. In consequence, there has always been a readiness on the part of the British manufacturer to improve the performance of his relatively small engine and obtain as much as possible from the "pint pot." The result of this is that there have been frequent and radical changes in British engine design and, often, completely new engines have been built to replace some having only an obsolescence of comparatively few years. This fact, together with the much smaller British home market in relation to the American market, has made the British car a more expensive proposition than the American vehicle. But it has taught us something about designing small engines to give relatively high power output with reliability.

Olley, in one of his informative papers, has said that the roads came before the motor car in Great Britain, whereas the reverse was the case in America. In fact, the principal towns of America were not linked by good roads until quite recently—between the two wars. Therefore, the Americans were able, at the start of the real motoring era, to build wide, straight roads entirely suited to fast motor traffic, and one can quite normally drive a hundred miles in two hours, in America, without exceeding a maximum speed of 60 m.p.h. Hence the large American engine which can cruise for long periods at a relatively low proportion of its maximum power.

The American car population is about fifteen times that of Great Britain with a correspondingly high car production of about 4,500,000 per annum, compared with Britain's 370,000. It will be appreciated, therefore, that the Americans cannot lightly change basic design, but have, until recently, relied upon styling and detail engineering changes from year to year, sometimes involving a major body and front-end re-hash.

This is not to suggest that the Americans have contributed little to the automobile. On the contrary, they have contributed a great deal and are world leaders in the production of low-cost automobiles of remarkable performance and reliability. Independent front-wheel springing was developed in America—incidentally by an Englishman, Olley. The pressed-steel and welded body, with its rigidity and freedom from annoying squeaks, was also an American development and replaced the old coachwork job which was the natural development from the days of horse-drawn vehicles.

Engine-design Considerations.

The horse-power tax, based on the old R.A.C. formula, has now gone, and this has largely freed the British car manufacturer in regard to engine-capacity limitations. But, although somewhat larger engines have since been designed and built, the size of car has altered little except in width, to make room for the occasional fifth passenger and, in some cases, to provide seating for three passengers in the front. There has been no swing to the American car or engine size, for the obvious reasons of overall operating economy.

Larger British cars are not expected in the quantity production class, *i.e.*, with engines of around 4 litres capacity, which is average for the American types. Relatively large engines of this type will, however, continue to be used in Britain in the so-called luxury car class, but world economy is such that the small and medium car will remain popular in Great Britain and other countries.

In any case, a very satisfactory car of medium size, to do the big car's job, can be built for a weight of about 28 cwt, having an engine of 2·5 litres in six cylinders. A reliable and tractable engine of this size could be designed to give a maximum or peak power of 100 b.h.p. at, say, 4500 r.p.m. and, more important, an output of 50 b.h.p. at maximum torque conditions at about 2000 r.p.m. The stroke–bore ratio of such an engine would be square (1 : 1) or nearly square (1·1 : 1).

The engine would be designed to give this performance with a compression ratio of about 6·75 : 1 on a fuel of 70 octane rating motor method with, say, a research appreciation of five numbers, *i.e.*, 75 octane number, research method.

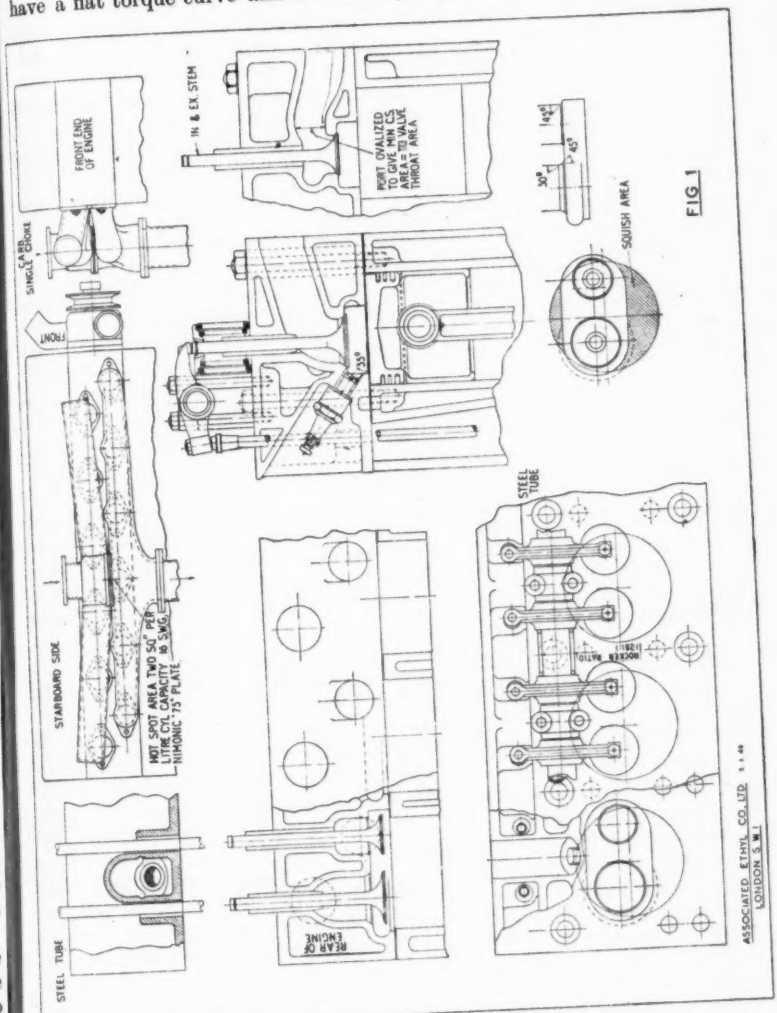
In Fig. 1 are given sketches of the general cylinder-head design of this engine. The " bath-tub " variety of combustion chamber is used, and a certain degree of squish turbulence, directed towards the sparking-plug, is provided. The offset " bath-tub " design also enables the compression ratio to be raised without upsetting combustion-chamber compactness, and when higher anti-knock fuels become available (outside the States) it will be possible to raise the compression ratio from 6·75 : 1 to, say, 10 : 1 without radical changes to the engine.

The scantlings of the main structure of the engine would be designed in the first place for rigidity, to ensure a smooth-running engine when high compression ratio is used. Allowance would also be made in the design of the main-bearing housings to take a larger or torsionally stiffer crankshaft, when changing to the higher ratio.

Some designers and manufacturers in Great Britain have considered it worth while to go to the twin-overhead-camshaft arrangement, with valves at a wide angle in a hemispherical combustion chamber. But any operational improvement effected by this arrangement would not appear to be entirely justified by the increased manufacturing cost, and it has little attraction for the quantity production car. The question of engine maintenance and overhaul, in service, is very important and, apart from the side-valve engine, which offers some advantage in this respect but is now out of date because of valve and compression-ratio limitations, the push-rod-operated overhead-valve engine would appear to be the best compromise on all counts.

There is also the hybrid " F "-head engine with the inlet valve in the head, over the cylinder bore, and side-by-side exhaust valves. The advantages of this arrangement are that it allows a large inlet valve to be used, unhampered by the proximity of the exhaust valve, and it also makes for a shorter engine. But it is difficult to avoid a relatively long and narrow or attenuated combustion chamber. Further, the exhaust valve is not in the best position from the point of view of good cooling and the avoidance of stresses tending to distort its seating in the cylinder-block, which can also affect the upper part of the cylinder bore.

It is submitted that the 2·5-litre engine represents the optimum size and would be economical to build and to operate. This engine would have a flat torque curve and a relatively high b.m.e.p. of over 130 p.s.i.



The value of the highest possible b.m.e.p. allied to the highest practicable compression ratio, to improve fuel economy, is not always appreciated, but it is necessary to have both to get the best results, although with both high compression and high b.m.e.p., there is risk of engine roughness, which must be countered in the engine and crankshaft design.

If there is any criticism of the excellent work done by the General Motors research laboratories on their 12·5 : 1 compression-ratio engine,[2] it would be that the b.m.e.p. is rather low for the very high ratio used and, in consequence, the economy of this particular engine is not so high as it could have been.

Another important point to appreciate in modern engine design is to avoid at all costs siamesed ports and, in particular, siamesed exhaust ports. They are bad for the cooling and stressing of the cylinder-head and tend generally to have an adverse effect upon exhaust-valve condition and life. The best arrangement is to have separate inlet- and exhaust-valve ports, arranged alternately in the cylinder-head. This arrangement allows better cooling of the exhaust valve.

Extraordinary to relate and despite the inference in the title of this paper, there has been no real attempt, to date, to design a "lead-proof" engine or one which takes full advantage of all the detail engineering improvements of the last twenty years or so, even although present engines of somewhat ancient design and considerable obsolescence are now fitted with better exhaust valves and sparking-plugs, which help to give improved engine life despite their uncongenial surroundings. Also, it is not necessarily the case that an engine, if designed and built to be proof against mechanical troubles arising from the use of leaded fuel, would be able to take full advantage of high anti-knock gasoline. Tetra-ethyl lead and high anti-knock value are not necessarily related and, outside the U.S.A. to-day, lead is being used mainly to improve low-octane gasolines and raise them to a value which is still hardly acceptable to existing engines. That is why an engine (of 2·5 litres) is suggested, designed in the first place to give a good performance on relatively low-octane gasoline and in which the compression ratio can later easily be increased, if and when better fuels become available.

In my view, great attention must be paid in any new engine design to the cooling of the whole combustion chamber and, as Kettering puts it, the engine must have more "built-in octane numbers," so that it will not need a gasoline of more than 80 octane motor method or, say, 86 research method to give a fuel economy of 20 to 25 per cent better than the average of to-day. The General Motors high-compression engine gives about 35 per cent improvement in fuel consumption on the road, but it requires a gasoline of 90 octane number motor method and 100 octane research method to achieve this.

It could be argued, as Kettering has done, that if there were a large number of cars in use with such engines, the overall and national saving in gasoline would be very considerable. An enormous capital expenditure would be necessary to equip the refineries to produce a sufficient quantity of really high-octane gasoline for this type of engine. A fraction of this expenditure, if devoted to engine research and development, could eventually result in a motor which would show the same high economy for, say, 8 or 10 octane numbers less than the fuel at present necessary for good operation at 12·5 : 1 ratio.

This is pure conjecture, but it is probable that the countries outside the North American Continent will not see generally distributed gasolines of, even, 80 octane number motor method for some years.

The recent high-compression work of General Motors research is almost a classic in showing how the economy of an engine can be practically improved and how the use of a very high ratio does not detract in any way from the smoothness of the engine, when it has been properly designed for high compression in the first place.

The General Motors research engine not only gave at least 33 per cent improved economy over and above the average car engine but also the extra power resulting from high compression allowed a smaller engine to be used. The General Motors 12·5 : 1 ratio engine has a cylinder capacity of 181 cu. in. (3 litres) in six cylinders and was compared in all road tests with a standard type six-cylinder side-valve engine of 238 cu. in. (3·9 litres). The compression ratio of this latter engine was 6·4 : 1.

These two engines were fitted in cars of the same type and weight (4000 lb). At 40 m.p.h., the fuel consumption of the standard car was 18·5 m.p. U.S.G. and that of the high-compression car 26·5 m.p. U.S.G., representing an improvement of over 40 per cent. There was a 35 per cent saving in fuel consumption at 60 miles per hour.

Data on a large number of trips with widely varying road conditions showed that the average gain in fuel economy for the high-compression car was 33 per cent, where both cars accompanied each other.

When the maximum speed was held below 50 m.p.h. the gain was 35 per cent and, when limited to a maximum of 70 m.p.h., a 33 per cent improvement was recorded. Kettering reports that several extended trips were made entirely in city traffic and showed gains of over 40 per cent. This is very important, since the highest car concentration is in and around the cities of the world and, therefore, most of the total fuel is burned and used in high-density traffic conditions, which are by no means ideal for best economy.

The scope of this paper does not cover the important question of operating economy in detail, but reference should be made to Kettering's paper [2] and to Campbell, Caris, and Withrow.[3]

The Effect of Tetra-ethyl Lead and its Scavengers upon the Engine.

The effect of adding tetra-ethyl lead to gasoline and the characteristic shape of the knock rating or octane-number curve, with increasing lead concentration, is well known and need not be discussed in detail here. But, for those who are not normally concerned with fuel matters, it is sufficient to say that the curve has a flattening characteristic or, in other words, it follows the law of diminishing returns. Some lead-response curves are given in Fig. 2.

The various gasolines also differ in lead response according to their particular chemical composition. It is common knowledge, too, that fuels of different chemical composition but of the same laboratory knock rating (octane number) will behave differently, one from the other, in an automobile engine or in an aviation engine. Furthermore, two different engines or even two engines of the same type will, because of differences in design or in manufacture, perform differently on the same fuel. The actual value of the octane number of any fuel improves with increasing

octane number, up to 100. In other words, an increase in octane number between, say, 80 and 100 is worth more in actual anti-knock value and permissible engine performance than a similar increase between 60 and 80 octane number. This, however, should not be confused with the flattening characteristic of the lead-response curve, which holds good for all gasolines, but shows that the octane scale represents a yardstick rather than an absolute measurement.

Apart from these characteristics, it has been found that certain of the sulphur compounds, particularly the polysulphides, the disulphides, and the mercaptans, have a depressing effect upon the lead response and the knock rating of motor gasolines. They were also found, in the recent war, to have similar and more marked effect upon the rich-mixture performance of aviation fuel, although they affected less its CFR motor

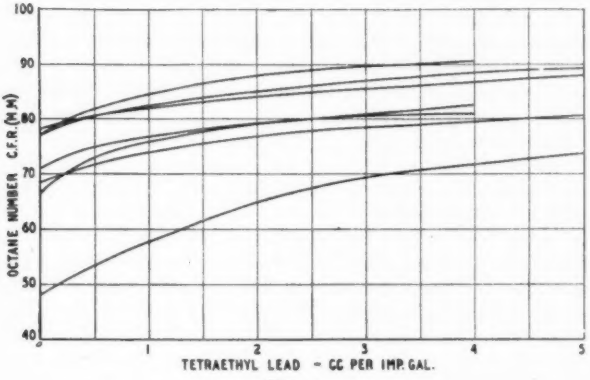


FIG. 2.

method rating. But it is interesting to note that thiophene has little or no effect upon rich-mixture performance.[4]

To continue the discussion on the effect of lead and its scavenging agents upon the engine, it is safe to say that, in general, no harmful effects need be expected from the everyday use of leaded fuel in the modern engine, nor has there been any real evidence of it seriously affecting the operating parts of the engine other than the exhaust valve and the sparking-plug, which parts are now mostly resistant to lead attack. Lead has sometimes been blamed as the contributory cause of other troubles connected with the lubricating oil and with sludge and deposit formation and accumulation. There has been little evidence to confirm that these are epidemic and, therefore, no trouble need normally be anticipated in this direction, when using leaded fuel. Naturally, lead compounds will be found in the lubricating oil and also in the sludge and other engine deposits, but they appear to do no harm.

The demands of the modern car have caused to be developed various additives for the fuel and for the lubricating oil. There are, for instance, gum inhibitors in the fuel and E.P. additives for the oil and, also, detergents to prevent the accumulation of deposits. All these have, at some

time or other, been suspected of causing odd troubles in the engine, such as bearing corrosion, etc., particularly where no other reasonable explanation could be given. It has also been thought that some of these troubles have been caused by interaction between an additive and the combustion products of leaded gasoline. This is quite possible, but the whole problem of additives and their interaction and effect upon the engine is of such complexity that, in the event of trouble, it is almost impossible to know whether or not the lead compounds are involved. In any case, although there have been sporadic troubles or small epidemics, attributed to the various additives, in recent years, in the States, it is not considered that leaded gasoline is the real offender and, normally, no trouble need be expected from this particular source.

Sparking-plug and Exhaust-valve Technique.

It will have been understood that the sparking-plug and the exhaust valve are the two components of the engine whose condition and operation can be adversely affected by leaded fuel, but there need be no apprehension in regard to the other engine components in this respect.

A whole lecture could be written on the subject of the sparking-plug and its development, but it is sufficient to say here that the progress made in the last ten years or so is such that the sparking-plug is no longer a real problem in the case of the automobile engine running on leaded fuel.

So far as the choice of a suitable plug is concerned, one which operates at as high a temperature as possible, within the limits of detonation and pre-ignition, is advised. Such a plug will then keep clean under all engine conditions and will tend to volatilize the lead compounds resulting from combustion.

Practically all, if not all, plug insulators for automobile and aviation engines are now of sintered aluminium oxide, which material is very resistant to lead attack. Each plug manufacturer has his own manufacturing trick in regard to the preparation and firing of aluminium oxide and its binder. The binder used is generally some form of clay and, because of this, care must be taken to keep the silica content as low as possible, because silica will combine with the lead to form a glass or glaze, which produces a conductive surface and will break down under running conditions; although, at room temperature, the plug may spark quite satisfactorily. Most manufacturers try to keep the silica content to within 4 or 5 per cent for aviation plugs, but it is often allowed to go above this figure, by double or even two and a half times, in automobile plugs. This type of insulator is fired in a gas kiln at between 1500° and 1700° C.

The sparking-plug boss in the cylinder-head should be well cooled, and it is not normally advisable to " pocket " the plug in the head. But the plug end, when screwed home, should not project into the combustion chamber, nor should there be any exposed threads.

Mica as a plug insulator was, for all practical purposes, discarded some years ago and is not now used for the automobile sparking-plug. Both the mica and the porcelain type of insulator were used for automobile plugs before the development of aluminium oxide as an insulator material;

and aluminium oxide started to displace mica for the insulator of the aviation-engine plug just before the recent war, when the high-duty operation of this type of engine was causing the mica to disintegrate, mainly due to its dehydration and chemical attack by the lead compounds.

The electrode and earth wires of the modern automobile plug are usually of some high-nickel alloy, but those which have been developed for the aviation plug in Great Britain were originated by K.L.G. and are of platinum alloy in the form of fine wire.

So much for the sparking-plug. Now for the exhaust valve, which still demands some attention to ensure long life under present-day running conditions.

For many years and between the two world wars, automobile-engine designers appeared to ignore the exhaust valve and seemed merely to regard it as a necessary evil, to let the exhaust gases out of the cylinder at the right time in the working cycle. There was little or no attempt made to cool the valve seating in the cylinder properly, and differential expansion occurred which set up severe stresses and caused its distortion. This, in turn, gave rise to gas leakage and burning of the valve, regardless of the fuel used. More often than not valves were bought by the many thousands, against no particular material or manufacturing specification. In fact, in some cases "bumped up" iron railing might almost as well have been used!

It was the aviation engine that influenced and hastened exhaust-valve development and the provision of better materials and improved valve and porting design.

The sodium-cooled valve, originated by Heron, was an effective attempt to improve exhaust-valve life, and to delay the onset of detonation and pre-ignition in the aviation engine. This type of valve is now universally used in the aviation engine. It is also generally employed in the States for high-duty bus and truck engines. Due to the small size of the automobile exhaust valve, particularly in British engines, it is difficult, although not impossible, to get any real benefit from sodium cooling in this particular case.

There is also the single-sleeve valve of the Burt type, which is proof against lead attack, but does not appear to be a practical development for the automobile engine, although it has an acknowledged place in the aviation engine as a result of the work done on it by the Bristol Aeroplane Company. However, the ordinary poppet valve now works quite well when care is taken in the design stages, and if the better valve materials available to-day are used.

In the past a categoric answer to the question: "Does lead cause exhaust-valve burning or not?" was expected. A straight "Yes" or "No" cannot be given, but the correct answer is that, all other things being equal, there is more risk of valve burning with leaded fuel than with clear gasoline. At the same time, it must be appreciated that tetra-ethyl lead has been largely responsible for better fuel uniformity, in respect of anti-knock value, which otherwise might have been impossible to achieve, particularly when considering the enormous quantities of gasoline now used. And the cases of valve burning, due to leaded fuel, have represented a surprisingly small proportion of the total vehicles in

service. There has also been a good deal of sheer prejudice and ignorance, rather than technical sense, behind some of the complaints blaming lead as the cause of the trouble. In fact, the general use of leaded fuel has brought about a vast improvement in valve technique and, consequently, in valve life, and the exhaust valve of to-day is much more reliable than that of ten years ago, and far ahead of anything available before the coming of leaded fuel.

The requirements for an exhaust-valve steel are that it must be resistant to temperatures between 700° and 800° C. It must resist hot-corrosion attack by the combustion products of leaded fuel, and it must also have resistance to cold corrosion or rusting, which can occur when the engine is at rest and is due to condensed lead compounds combining with the water condensate, to form acid products.

Exhaust-valve steel must be easy to forge and should not be subject to "hot shortness" or to brittleness. At the same time, the valve stem should have some degree of hardness to provide good bearing surface and contact with the valve-guide material.

There are a number of improved steels which have been developed specifically for exhaust valves and which go a long way towards meeting these requirements. Details of some of these are given in Table II.

TABLE II.

Material.	Cr.	Ni.	Si.	Mo.	Mn.	C.	Fe.	Brinell hardness at 760° C.	Remarks.
Silcrome XB (EN. 59) .	21·0	1·5	2·0	—	0·40	0·75	Bal	75	—
XCB . .	23·75	4·75	1·0 max.	2·75	1·0	0·45	,,	210	—
2112 . .	21·0	12·0	0·80	—	1·4	0·20	,,	110	—
2112 N .	21·0	12·0	0·85	—	1·2	0·20	,,	—	0·18% nitrogen in this steel
XCT . .	24·5	6·5	0·40	4·25	0·90	0·40	,,	230	—
DTD 49b .	12·00–16·00	10·00	2·00	—	1·50 max.	0·45	,,	—	W 2·00%–4·00%

When the automobile manufacturers started to pay attention to the exhaust valve, a few years before the recent war, there was developed a steel which was then far ahead of the types of nickel steels used previously. This steel was known as "Silcrome No. 1" and contained about 3·5 per cent silicon and 8 per cent chromium. But the demands of present-day road performance have now outstripped the ability of this steel to resist the higher duty, and it has been replaced by one or other of those given in Table II.

"Silcrome XB" steel (No. 1 in Table II) has been generally used in America for some years, although it is only just coming into use in Great Britain. Now, in America, "XB" is in turn being replaced by "2112" material and, also, "XCR." "2112" is more favoured than "XCR" because it is easier to produce, although "XCR" gives excellent results in the engine.

Valve-facing materials such as Stellite, Brightray, and Eatonite are used for all high-duty exhaust valves, in aviation engines, and in buses and trucks. But they are expensive for the average motor-car engine, although some of the higher-priced cars use them.

There is a move to consider a valve of two-piece construction having a head of fully austenitic steel (of the D.T.D. 49b variety) or of non-ferrous alloy such as Brightray, welded to a stem of suitable corrosion-resisting steel of good tensile strength and hardness. However, the manufacturing costs of the two-piece valve are likely to be somewhat higher and, because of this, any technical advantages must be weighed against the increased cost.

Stellite was first used for the aviation-engine exhaust valve because of its hardness and resistance to lead attack. But as engine duty increased it was found that Brightray had superior resistance in this respect and it replaced Stellite, although it is much less hard than the latter. Recently, Eatonite has been developed, which is also hard and appears to be superior to these two materials in some cases. Most aviation exhaust valves are coated over the head as well as on the face with such materials (usually Brightray) to avoid attack and scaling of the head surface. The valve-

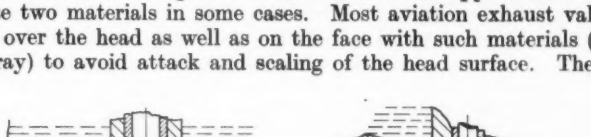


FIG. 3.

insert seating ring in the cylinder-head is also generally treated with hard, corrosion-resistant material such as Stellite or Eatonite, but a Brightray type of material is now being tried for the insert, otherwise untreated.

Valve-seat inserts are universally used for the aviation engine and for bus and truck engines, but they are not in general use for the automobile engine because of its lower duty operation and the lack of room to fit them, in the smaller cylinders. Inserts are not always faced with Stellite, but are often made of the special irons or of tool steel, and depend mainly upon the hardness of the material and the relatively low temperature of the cylinder-block in resisting hammering, sinkage, and hot-corrosion attack.

The design of the exhaust valve and that of its seating and porting in the cylinder-head or cylinder-block must aim to avoid a valve temperature exceeding 700° C under all running conditions, *i.e.*, the temperature should not rise above this figure at any point on the valve face. If it does, and once burning starts, the results are cumulative. Ideally, the temperature should not exceed 650° C, but this may not be practically possible in the case of the average car engine.

In Fig. 3 are given examples of exhaust-valve and port design—(*A*) is good and (*B*) is bad. In the case of (*B*), it will be seen that there is little bossing for the valve guide, which projects into the port and merely acts

as a heat trap. The engine coolant is also somewhat remote from the valve seating and from the guide. These points have been rectified in the case of (*A*), taking advantage of a smaller exhaust valve relative to the inlet valve, which is particularly permissible in the case of unsupercharged engines.

The valve guide should not normally project beyond the bossing in the port, but this has sometimes been done deliberately in the case of those engines which suffer continually from valve sticking, so that it can act as a heat shield for the valve stem immediately above the valve neck. In such cases, large clearance is given between the projecting part of the guide and the valve stem, but the guide has limited life and must be renewed at regular intervals.

To avoid valve sticking, the guide is sometimes counter-bored at its port end to give a fairly large clearance or, conversely, the valve stem is made somewhat larger in diameter, for the equivalent guide length. This makes a step in the valve stem at the porting end of the guide. The step is given a sharp edge and is retracted into the guide when the valve is in the closed position. When the valve is opening, the step acts as a reamer and keeps the mouth or entrance of the guide clear of any deposits which might cause sticking. See Fig. 3 (*A*).

Referring to the cylinder-head and combustion-chamber sketches shown in Fig. 1, it will be noted that the exhaust valve is somewhat smaller than the inlet valve. In practice, and for naturally aspirated engines, the effective port area of the exhaust valve can be some 60 per cent of that of the inlet valve, without markedly affecting cylinder scavenging and engine performance. There are three distinct advantages in using the smaller exhaust valve. The first is that it removes any restriction upon inlet-valve size, for the latter to give good cylinder filling and high volumetric efficiency. The second advantage is that it allows better scope for the designer to design and the foundry to reproduce adequate coolant passages, for the better and more uniform cooling of the valve seating and guide. The third point is that the smaller exhaust-valve head reduces the amount of uncooled surface exposed in the combustion chamber and so helps to reduce the octane-number requirement of the engine.

Valve Rotation.

Apart from the questions of better valve steels and superior engine design, there has been a very interesting development, in the States, to improve exhaust-valve condition and to give longer valve life. This concerns the rotation of the valve under running conditions, which is effected by a fitment at the tappet end of the valve stem.

There are two devices which have been developed for this purpose. One is known as the non-positive valve rotator, and the other, the positive rotator. Sketches of these are given in Fig. 4.

It will be noted that the non-positive rotator (*A*) takes the form of a cap fitted over the valve-stem end with small clearance between it and the stem end when the valve is closed. When the cam starts to take up the clearance, preparatory to lifting the valve, the cap bears on the keep of the spring retainer or collar and thus relieves the valve of the spring

load. The vibration of the engine then allows the valve, in this short "free" period, to turn or rotate a degree or so. When all clearance has been taken up, the valve opens in the normal way.

In the case of the positive rotator (*B*), this imparts to the valve a positive degree of rotation at every operation of the valve and does not depend upon engine vibration or the gas-flow conditions around the valve head, to impart rotation. It will be seen from the sketch (*B*) that this rotator combines in it the valve-spring-retaining collar, consisting of a shell or main body of two-piece construction, in which there are a number of small steel balls (*C*) kept in position at the upper ends of inclined planes or ramps by light springs. Interposed between the two pieces is a flat spring washer (*B*) of the Belleville type. When the cam starts to lift the valve, and the spring load increases, this flattens the spring washer on to the steel balls and forces them down the ramps, causing the retainer (*D*) to turn a small amount and so rotate the valve.

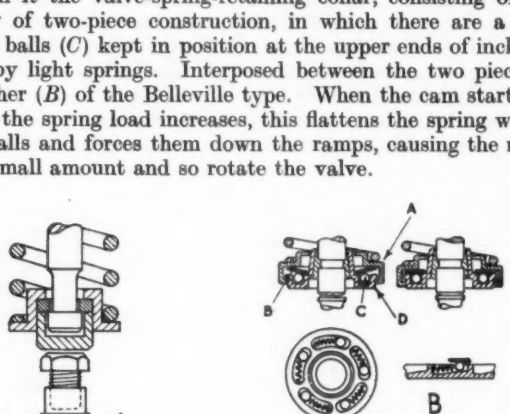


FIG. 4.

Rotation has probably contributed more to improving the exhaust-valve condition and life than any other development of the last twenty years, and some remarkable improvements in running times have been recorded.

The idea of valve rotation is about thirty years old. When it was first thought of there were many difficulties preventing its successful use, such as excessive valve-seat wear and valve-stem breakages.

Stimulated by the U.S. Army Corps of Engineers, who were interested in getting better valve life, particularly from stationary engines under severe Service conditions, the Ethyl Corporation, of America, undertook a large-scale co-operative rotator test programme in 1943, in order to judge the worth of valve rotation in ordinary practice.

A summary of the results and conclusions of these tests by the Ethyl Corporation has shown that valve rotation, in conjunction with Stellite or Eatonite hard-faced valve seats, "substantially extends exhaust valve life in commercial vehicles and stationary engines. Rotation has so improved the exhaust valve condition that it now matches piston ring life in a wide variety of engines."

Rotation improves valve life because it eliminates valve sticking and reduces considerably the deposits on the valve face and the seat. The intermittent rotation of the valve also avoids the localization and concentration of heat at any one point of the valve face. This is particularly

the case where there is some distortion of the seating in the cylinder-head, or block, which gives rise to gas leakage. The stems of valves which have rotated are clean and polished in appearance, and the valve seats are practically free of deposit.

Hard-faced valves are necessary in the case of high-duty operation, where valve rotation is used. For light-duty engines, rotation has been successfully applied without this treatment of the valve seat.

There appears to be little or no difference in the valve condition between the non-positive and the positive rotator, and both seem to give equally good results so far as valve life is concerned.

These conclusions are based on 163 tests by the Ethyl Corporation, involving a wide variety of engines, fuels, lubricants, maintenance, types of service, and geographical locations. The tests involved more than seven million vehicle miles and greater than 12,000 hr of stationary-engine operation. The lead concentration of the fuels used ranged from 0·6 to 2·6 cc per U.S.G., or 0·72 to 3·1 cc per I.G.

It is interesting to note that valve life was not, apparently, related to the lead concentration of the fuel in these rotator tests, which is some proof that, where the valve condition is well outside the borderline of trouble, increasing lead concentration, even above the normal average amount, does not appear to bring it within the borderline or cause a corresponding reduction in valve-operating life.

Before leaving the subject of the exhaust valve, it should be recorded that the Thornton Laboratory of Shell have been developing a new treatment for the valve face and head, to give increased resistance to hot-corrosion attack by the combustion products of leaded fuel. The treatment consists of the application of a layer of alloy composed of nickel, cobalt, and aluminium (Ni–Co–Al) to the valve head. According to Thornton, the best way of applying the layer is to immerse the valve head in the molten alloy. Special means are taken to ensure that reaction occurs between the alloy and the valve material, for bonding purposes, which is followed by a diffusing treatment to produce homogeneity in the bonding of the alloy and valve material.

This method of treating the valve is still in the experimental stage and has been developed, by Thornton, mainly for aviation-engine valves. It is believed that the alloy is now applied to the valve after the latter has first been faced with a hard material such as Stellite, Eatonite, or the new Rolls-Royce C.26 material. Apparently, the effectiveness of this alloy depends upon the formation of a stable and refractory oxide coating on the surface of the alloy layer.

Lead Scavengers.

The need for scavenging the lead compounds from the engine, after the lead has done its work, became apparent very early on, if not almost immediately after leaded fuel was first tried in an engine. Ethylene dibromide and ethylene dichloride, since their discovery as scavengers, have continued to be used, but the search for still better scavengers goes on, although nothing has yet been found sufficiently satisfactory to replace these two compounds.

The principal requirements for a new scavenger are as follows :—

1. It must obviously be a better chemical scavenger and remove the lead compounds more efficiently than those in use at present. In doing this there must be a marked reduction in cylinder deposits, particularly as they affect the exhaust-valve and sparking-plug condition.

2. It now appears that the vapour pressure of a scavenger should be as near as possible to that of tetra-ethyl lead, to ensure equitable distribution of the lead and scavenger, with the fuel, to the engine cylinders. So far, however, this feature has only been apparent in the case of aviation engines with the in-line cylinder arrangement.

3. The scavenger must be completely miscible with tetra-ethyl lead and also with the gasoline.

4. It must be stable in storage, in normal and in tropical conditions, both in the concentrated form, with lead, and when blended with gasoline.

5. The freezing point must be no higher than that of, say, ethylene dibromide and, preferably, much lower.

6. The production cost of any new scavenger should not be greater than that of the present compounds, although this is unlikely to be realized in practice. But it must combine marked improvement in efficiency of action with reasonable production cost.

These requirements tend to conflict with each other because scavenging efficiency (1) may demand a certain degree of chemical instability of the scavenger, in order to get quick reaction between it and the lead, and this might be detrimental to storage stability (4), particularly in tropical conditions.

There is another consideration in connexion with the action of the scavenger in the engine cylinder. If its reaction with lead is too rapid, then it may well devour or destroy the lead before the latter has time to be effective as an anti-knock agent. It has been known for some time that the scavengers have this effect upon the lead. The lead-response curve of a given gasoline, when made with lead only and without the scavenger, shows a lower lead requirement, *i.e.*, less lead is required for a given increase in octane number, than the same gasoline when both lead and scavenger are added.

It will be appreciated, therefore, that it is not at all easy to find a scavenger having the chemical balance which combines all these requirements and advantages.

Now follows a condensed description of some work which has been done in Great Britain, mainly during the recent war, on lead and scavenger distribution to the cylinders of aviation engines having the in-line cylinder arrangement.

During the war, severe sparking-plug fouling was experienced with Rolls-Royce Merlin and Allison engines. This trouble occurred in relatively long-range operations where, to achieve range, the engine was run at very low cruising power and, therefore, at much reduced boost and speed (r.p.m.). Because of the low boost or mixture temperature the fuel distribution to the cylinders was upset, causing a variation in the

mixture strength to the different cylinders or groups of cylinders. In addition, the lead concentration in the fuel to each cylinder also varied. The halogen bearer or scavenger, ethylene dibromide, was fairly equally distributed to the cylinders, but, since the front-end cylinders were receiving the largest quantity of lead, there was only sufficient scavenger present to convert a very small proportion of the lead and, in consequence, a heavy deposit built up in these cylinders, causing plug fouling and some exhaust-valve burning.

Bench tests were then run under simulated flight cruising conditions, and the Ministry of Aircraft Production also sought the technical assistance of the Thornton Laboratory of Shell, which had been offered by Shell to the Ministry for the duration of the war. It was found, from exhaust-gas analysis of the individual cylinders (a method developed by Thornton), that the heavy or heavier ends of the fuel went to the front-end cylinders, carrying most of the lead with them, and the lighter fuel ends were distributed to the remaining cylinders.

The results of some of these tests were interesting, in showing the actual distribution of the lead. The fuel used was 100/130 grade containing 7·2 cc of lead per Imperial gallon. It was found that the lead concentration in the fuel varied from cylinder to cylinder, in the following manner :—

1. On the left cylinder bank, No. 1 cylinder (front) received 4·9 cc T.E.L./Imp. gal; No. 2, 5·3 cc; No. 3, 5·3 cc; No. 4, 5·0 cc; No. 5, 6·3 cc; No. 6, 5·2 cc.
2. On the right cylinder bank, No. 1 cylinder (front) received 12·1 cc T.E.L./Imp. gal; No. 2, 9·8 cc; No. 3, 10·2 cc; No. 4, 6·3 cc; No. 5, 6·6 cc; No. 6, 6·7 cc.

Nos. 1, 2, and 3 cylinders on the right bank not only received a large amount of lead but, in view of the equitable distribution of ethylene dibromide, they received also the lead in the form of 0·5 theory mix or only about half of the scavenger required to combine with the lead. Furthermore, the octane number of the fuel delivered to No. 2 cylinder on the left bank was only 95, whereas that delivered to No. 1 cylinder on the right bank was better than 103 octane.

When the results of a number of tests confirmed that the lead followed the heavier fuel ends into the same cylinders, it was reasoned that the scavenger might accompany the lead better if its boiling point or vapour pressure approached more closely to that of the lead. Resulting from this, the Thornton Laboratory suggested acetylene tetrabromide as an alternative to ethylene dibromide, because the volatility of the former approached more closely that of the lead.

Many hundreds of engine hours, on the test bench and in flight, indicated that this theory was at least along the right lines and that acetylene tetrabromide well satisfied the needs. Sparking-plug fouling did not occur under the same cruising conditions, and the valve condition was good. Most unfortunately, however, acetylene tetrabromide proved to be unstable in storage, particularly under simulated tropical conditions, so that it had, regretfully, to be discarded.

A disturbing feature which marked the laboratory tests was the con-

siderable temperature rise which occurred when this material was mixed with tetra-ethyl lead, thus indicating that there was interaction between acetylene tetrabromide and tetra-ethyl lead which might cause dangerous instability in storage.

Some further storage tests were arranged by the M.A.P. under actual tropical conditions, with drums of aviation fuel containing fluid having acetylene tetrabromide as the scavenger. After some months, the drums were opened and inspected, and considerable corrosion of the inside of the drum was found to have occurred in the air space above the fuel level. These results finally eliminated acetylene tetrabromide as a scavenger, which was a great pity because it behaved excellently in the engine.

Since then, Rolls-Royce have developed automatic control of the induction-pipe temperature where, under low-power cruising conditions, the mixture temperature is kept at not less than 40° C and, preferably, 45° C. This has had the effect of re-establishing good fuel distribution to all the cylinders, with normal "aviation mix" fluid containing ethylene dibromide, without re-occurrence of the plug-fouling trouble.

Tests in automobiles with similar scavengers, for reasons yet to be fully understood, have not given the same results, and no particular improvement in engine (valve and plug) condition has been noted when compared with the present scavengers used in "motor mix" fluid. This is, however, generally understandable because of the varying load operation of the automobile engine, which differs completely from that of the aviation engine. Also, in the former case, the induction pipe is much smaller in size and in length, and there is no supercharger. Short induction-pipe length probably has considerable, and favourable, effect upon the fuel distribution in combination with that of the lead and its scavenger. There are not the quantitative differences in the distribution system of the automobile engine compared with the aviation engine, although, of course, there will be some variation of mixture strength from cylinder to cylinder. But the large temperature variation in the cylinders of the car engine, because of its ever-changing load, puts severe demands upon the scavenger, which, ideally, should be able to convert the lead as efficiently at low load and low (cylinder) temperatures as at the high-duty condition.

If suitable chemical compounds were found, the selection and mixing with the lead of two different scavengers or scavengers differing in vapour pressure and designed to cover the whole engine-operating range might further improve the overall engine condition. The present "motor mix" fluid already contains two different chemicals as scavengers, but for somewhat different reasons. Should that particular part of the combined scavenger intended for the low-load condition do its job, it would be difficult to ensure that the other part intended for scavenging at high duty is also effective at the same cylinder conditions. If it is not, some may go largely to form deposits at low load, and that part which is effective at low load may be over-effective at high load and destroy some of the lead, thus reducing its value as an anti-knock.

Before leaving the subject of lead scavenging, it may be of interest to record that some other tests were done on aviation engines in Great Britain, during the war, and were repeated more recently in America,[5] where "1-T

Mix Aviation" fluid was replaced by one containing 1·5 theories of ethylene dibromide.

Since one theory of ethylene dibromide does not completely scavenge the lead compounds, it was thought that, by increasing the amount of scavenger, this might improve the scavenging process and so reduce the deposit amount in the cylinder.

The results of the British tests confirmed this, and much less deposit was present in the cylinders after many hours of endurance running on the Merlin engine. However, considerable erosion or sinkage of the valve-seat inserts occurred, and there was also prohibitive wear of the exhaust-valve guides.

The recent tests in America, along the same lines but with an air-cooled radial engine, confirmed the British results in almost every respect. But, in addition to valve-insert sinkage and valve-stem and guide wear, the American tests were marked by a relatively high rate of sparking-plug failure, which, with 1·5 theory fluid, increased from 4·8 per 100 operating hr to 10·3 failures per 100 hr. Droegemueller reports that, whereas lead fouling did not occur in this particular case, it was replaced by corrosion attack of the business end of the plug by the action of the bromide. Approximately one half of the failures were due to attack of the silver solder holding the centre electrode, which caused the latter to loosen and, in some cases, fall out. The lead, apparently, alloys with the silver to form a lower-melting-point material.

In Table III are given relevant data on 1-T and 1·5-T fluids and, in Table IV, the characteristics of some typical lead compounds which are present in combustion-chamber deposits.

TABLE III.

Data on Tetra-ethyl Lead Mixtures.

	Components.	
	Tetra-ethyl lead.	Ethylene dibromide.
Boiling point, ° C	197·0	131·7
Density, g/ml	1·659	2·18
Molecular weight	323·5	187·9
	Mixtures.	
	1-T fluid.	1·5-T fluid.
Weight per cent composition :		
Tetra-ethyl lead	61	52
Ethylene dibromide	36	45
Dye, impurities, etc.	3	3
Volume per cent composition :		
Tetra-ethyl lead	65	57
Ethylene dibromide	28	37
Dye, impurities, etc	7	6
Lead content, per cent	39	33
Bromine content, per cent	30	39
Sp. gr. at 20° C	1·746	1·801

TABLE IV.

Characteristics of Some Lead Compounds.

Compound.	Colour.	Melting point, °C.
PbO	Yellow to red	888
$PbSO_4$	White	999–1093
$PbBr_2$	Brown-white	371
$PbO–PbBr_2$	White	328–890
$PbCl_2$	White	499
$PbO–PbSO_4$	White	977

The author is in general disagreement with Droegemueller's outlook and feels strongly that it is defeatist, because he appears to assume that nothing can be done, so far as the engine is concerned, to alleviate the troubles of which he complains. At the same time, while admitting that we, in Great Britain, are not free from all trouble, we are certainly not

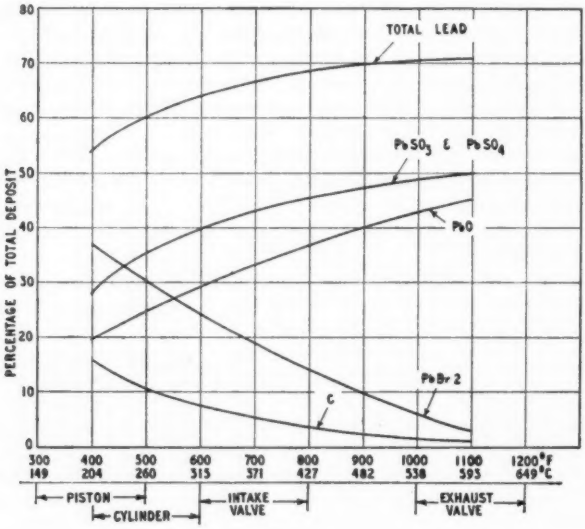


FIG. 5.

getting into the difficulties described by him. Droegemueller has, however, given some very useful information and statistical data. For instance, there is a family of curves giving the chemical analysis of the deposits, against temperature, taken from the various parts of the combustion chamber and piston head. These are reproduced in Fig. 5.

Simple arithmetic will show that about half a ton of metallic lead will have been supplied to an aviation engine, through the fuel, when it has run for 1000 hr at, say, an average power output of 1200 b.h.p. Further, Droegemueller reminds us that the various additives, including "Ethyl"

fluid, which are now put into aviation fuels, although very small in individual quantity, represent a fairly large amount of relatively non-volatile material passing through the engine during its operating life, between servicing periods; and he gives data showing the weight of material supplied to the engine, on the basis of 100,000 U.S. gallons of fuel used. This data is reproduced in Table V.

TABLE V.

Deposit-forming Material Supplied per 1000 hr.

Component.	Concentration.*	Material supplied, lb.
Metallic lead	4·6 ml T.E.L./gal	1000
Sulphur	0·05 per cent by weight	300
Gum	6 mg/100 ml	50
Inhibitor	1 lb/5000 gal	20
Dye	14 mg/gal.	3

* Maximum permitted by specifications.

The author's opinion is that, to assist the general scavenging of all deposits from the cylinder, particularly in the case of the automobile engine, the combustion chamber should be designed for a fairly high degree of turbulence. Although no specific tests have been seen to confirm this, it has been noted that those engines having a high degree of turbulence always appear to be cleaner.

This is all that can be said at present on the subject of scavengers, but it serves to show that the problems attending the search for any new and better scavenger are very considerable, and quick results cannot be expected.

CONCLUSION.

An attempt has been made to give an accurate historical account of the development of tetra-ethyl lead as an anti-knock agent and to discuss dispassionately the technical problems which have been associated with the use of leaded fuel in the automobile engine and in the aviation engine. The author's view is that these problems have now been largely overcome and epidemic trouble is not to be expected; since there is or should be a thorough understanding, by all concerned, of the technical requirements for " lead proofing " an engine.

Tetra-ethyl lead is now accepted as an essential material for use in the oil refinery, to help in reducing the refining costs; because it is generally cheaper to improve the anti-knock value of the fuel by adding lead than by the further processing of the fuel, which usually involves expensive refining methods.

The author wishes to acknowledge the Ethyl Corporation, of America, for the historical facts regarding the discovery of tetra-ethyl lead as an anti-knock specific and, also, for permission to use certain information on valve-rotation technique. He also wishes to thank his colleagues for their helpful criticism and advice, and The Associated Ethyl Co. Ltd., for permission to present this paper.

APPENDIX.

A Note on Pre-ignition.

There still appears to be some confusion in regard to the term pre-ignition, and the proper description of this phenomenon. Pre-ignition, by definition, is the ignition of the charge before the normal source—the spark—touches it off.

Ricardo has stated [1] that the observed maximum pressure in the engine cylinder, with pre-ignition, is not greater than that when the engine is operating normally; and Professor Hopkinson, with whom Ricardo was working at the time, gave the reason that there was only the same (charge) energy available in both cases. But higher maximum pressures, some 40 per cent greater than normal, have been recorded, with pre-ignition, in more modern (aviation) engines.[6]

The modern engine runs at much higher output and speed; and this higher peak pressure is explainable because, although the heat energy of the charge remains the same, earlier ignition of the charge probably results in a lower heat-rejection rate from the combustion-chamber surfaces; and the time factor, due to (higher) engine speed, may largely control this. In the case of Hopkinson's experiments, these were mostly done on a single-cylinder engine where, immediately pre-ignition took place, there was a marked reduction in engine speed, controlled only by flywheel inertia. But in the modern multi-cylinder engine where, generally, pre-ignition will probably only start in one of the cylinders, the engine speed is maintained for a much longer period and, by the time a reduction in engine speed occurs, due to pre-ignition, the conditions in the pre-igniting cylinder will have reached fairly destructive proportions.

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ALKYLNAPHTHALENES. PART IV. THE INFRA-RED ABSORPTION SPECTRA OF SOME MONO-ALKYLNAPHTHALENES AND THE DIMETHYL-NAPHTHALENES.

By E. E. Vago, E. M. Tanner, and K. C. Bryant.

Summary.

The infra-red absorption spectra of twelve α- and β-monoalkylnaphthalenes (methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl-, and *n*-hexyl-) and of the ten isomeric dimethylnaphthalenes have been measured in the region 700 to 1900 cm^{-1}. Characteristics of the spectra and possibilities of identification in mixtures are discussed.

Introduction.

During the course of an investigation into the composition of petroleum fractions boiling in the gas-oil range it became necessary to determine the concentrations of naphthalene and its homologues in distillation fractions.

The lowest-boiling members of the series, namely, naphthalene and α- and β-methylnaphthalenes, can be readily distinguished and estimated by ultra-violet absorption spectroscopy.[1, 2] With increase in boiling point, however, the homologues become much less readily identifiable. The ultra-violet absorption curves of the dimethylnaphthalenes were found to be very similar,[3] and this, with one or two exceptions, would make the detection of the individual compounds in a mixture of the isomers very difficult. The ultra-violet spectra of the higher monoalkylnaphthalenes bear an even greater resemblance to their α- and β-methyl homologues, although it is possible to differentiate between α- and β-compounds.

To ascertain whether infra-red-absorption spectroscopy would provide a more suitable means of analysing mixtures of higher-boiling alkylnaphthalenes it was first necessary to record the infra-red spectra of the individual pure naphthalenes.

Experimental.

(a) *Apparatus.*

The instrument employed for plotting all the infra-red spectra was a Hilger D.209 double-beam spectrometer[4, 5] using a 30° rock-salt prism with Littrow mounting and a Hilger–Schwarz double thermocouple. A Nernst filament was used as source. The outputs from the thermocouple, both "blank" and "sample" beams, were amplified separately in a Pye double D.C. feedback amplifier, and their ratio plotted by a Cambridge recording potentiometer. In this way a direct plot of percentage transmission, uncorrected for cell zero, was obtained from 700 to 1900 cm^{-1} on a linear frequency scale.

(b) *Procedure.*

The naphthalene derivatives measured were α- and β-methyl-, -ethyl-, -*n*-propyl-, -*n*-butyl-, -*n*-amyl, and -*n*-hexyl-, and the ten dimethyl-

naphthalenes. These were kindly supplied by Dr J. C. Smith of the Dyson Perrins Laboratory, Oxford, who has described their syntheses and physical properties in earlier papers.[3, 6, 7]

The spectra of the liquids were measured in rock-salt cells of about 0·1 mm thickness as well as in capillary layers formed by pressing a drop of the liquid between two flat rock-salt plates. Films of the solid compounds were prepared by heating two small rock-salt plates, placing about

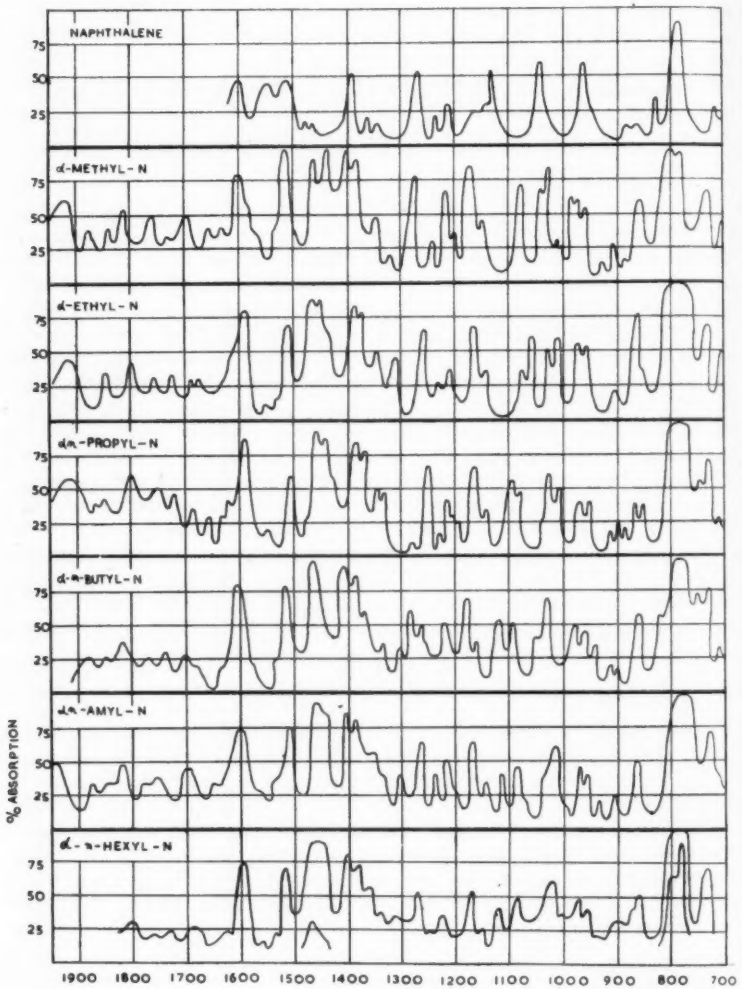

FIG. 1.

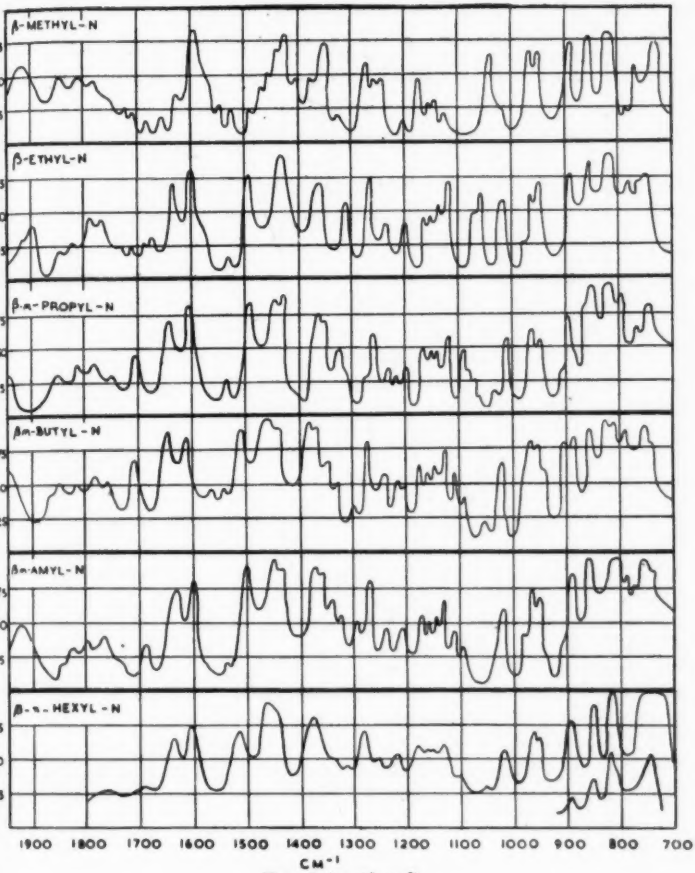

FIG. 1 (*continued*).

0·1 g of the solid on one of the plates, and then allowing the molten layer to cool with the plates pressed together. Naphthalene was not examined as a solid, on account of its short melting range, and deposition from a solution produced a highly scattering surface.

The spectra between 1350 and 1650 cm^{-1} of naphthalene, α- and β-methyl-, and the dimethyl-naphthalenes in dilute solutions in carbon tetrachloride were also recorded.

RESULTS AND DISCUSSION.

The spectra of the monoalkylnaphthalenes are reproduced in Fig. 1, the spectrum of naphthalene in carbon disulphide solution being included

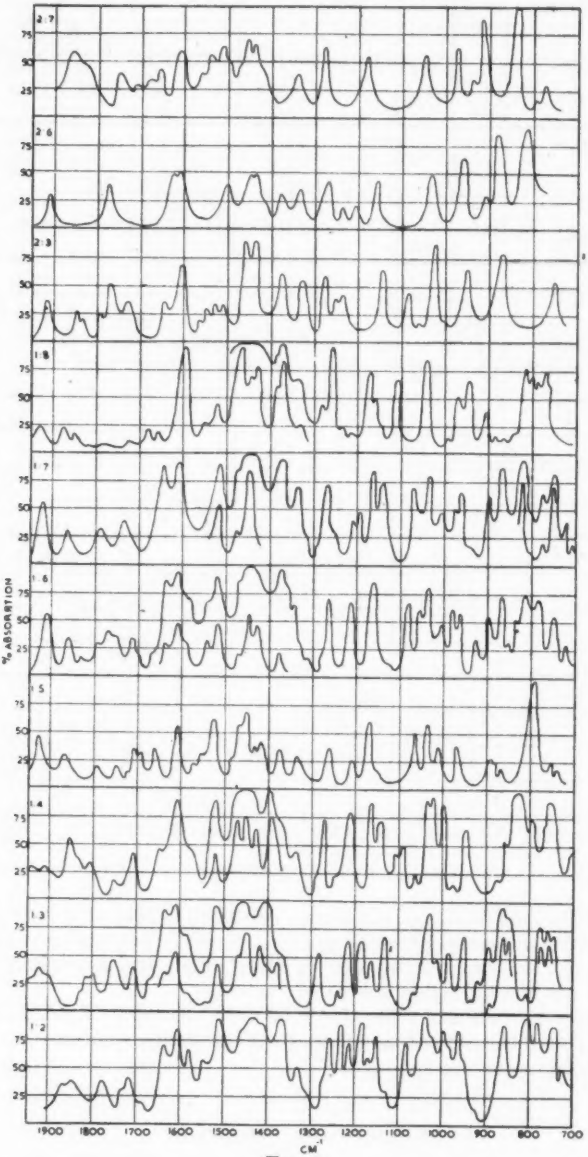

FIG. 2.

INFRA-RED SPECTRA OF THE DIMETHYLNAPHTHALENES.

for comparative purposes. The frequencies of the stronger bands are compared in Table I. As would be expected, great similarity can be observed among the spectra of both the α- and the β-compounds.

TABLE I.

The Stronger Bands of the Monoalkylnaphthalenes (14·5–6·2 μ).

Naphthalene.	1-Me-.	1-Et-.	1-n-Pr-.	1-n-Bu-.	1-n-Amyl-.	1-n-Hexyl-.	2-Me-.	2-Et-.	2-n-Pr-.	2-n-Bu-.	2-n-Amyl-.	2-n-Hexyl-.
—	698	696	698	698	698	696	—	—	—	—	—	—
—	733	732	732	732	732	732	732	750	744	752	755	746
786	776	783	779	779	779	781	—	—	—	—	—	—
—	796	803	789	793	793	795	818	818	814	818	(805)	820
—	856	851	850	860	865	859	856	854	848	857	857	854
—	903	904	908	908	903	903	892	890	893	888	890	896
959	953	953	952	958	953	953	953	947	946	953	952	952
—	972	967	965	976	968	969	964	964	958	961	963	962
1040	1026	1028	1026	1028	1018	1020	—	1018	1017	1022	1021	1021
—	1082	1059	1090	1093	1083	1085	1041	1057	1089	1090	1097	—
—	—	—	—	1119	1114	1120	1125	1122	1122	1130	1130	1132
1132	1146	1142	1138	—	1146	—	1145	1140	1139	1147	1145	1152
—	1169	1164	1160	1158	—	1150	1155	1153	1148	1159	1158	1161
—	—	—	—	1180	1168	1171	1174	1166	1164	1173	1171	1180
1209	1216	1211	1215	1220	1217	1225	1203	1200	1197	1203	1210	1219
1265	1270	1255	1250	1260	1264	1270	1272	1264	1262	1273	1268	1282
—	1381	1372	1364	1370	1350?	1358	1351	1361	1362	1377	1370	1378
1391	1397	1382	1379	1384	1386	1380	—	—	—	—	—	—
—	1436	1450	1441	1403	1406	1398	1423	1435	1429	1442	1434	—
—	1460	1460	1454	1464	1462	1466	1455	—	1442	1458	1452	1466
1512	1512	1508	1505	1517	1512	1515	1490	1528	1496	1513	1501	1516
1600	1599	1590	1589	1604	1598	1595	1595	1601	1607	1608	1598	1607

The spectra of the ten isomeric dimethylnaphthalenes are shown in Fig. 2, and the frequencies of their principal absorption maxima are listed in Table II. Direct comparison between these substances may not be justifiable, since some are liquids and some are solids and changes in the frequencies and intensities of absorption bands may occur with change of state. The frequencies between 1370 and 1630 cm^{-1} can often be correlated with particular vibrations,[8, 9] and they were therefore measured in carbon tetrachloride solution (see Table III and Fig. 3). Due to the low resolving power of the rock-salt prism in this region the frequencies can be taken as accurate only to ± 5 $cm.^{-1}$.

The following points may be noted:—

1. All these compounds have strong bands at about 1500 and 1600 cm^{-1}. It is interesting to find that these frequencies which have been interpreted in the benzene series as in-plane skeletal vibrations of the benzene nucleus[10] should appear almost unchanged in the naphthalene series.

2. 1 : 8-Dimethylnaphthalene is the only isomer in which there are two bands in the region of 1375 cm^{-1}, a frequency generally associated with the symmetrical deformation of the $-CH_3$ group. It is suggested that this is connected with the proximity of the two methyl groups which a scale model shows to be closer for this isomer than for any of the others. This steric effect may be the cause of a doubling of the frequency.

3. Attempts to correlate the variations of the spectra in solution in carbon tetrachloride in this region with symmetry properties of the molecules were unsuccessful.

TABLE II.

The Stronger Bands of the Dimethylnaphthalenes in the Region 14·5–7·9 μ.

1 : 2-Me_2N, liquid.	1 : 3-Me_2N, liquid.	1 : 4-Me_2N, liquid.	1 : 5-Me_2N, solid.	1 : 6-Me_2N, liquid.	1 : 7-Me_2N, liquid.	1 : 8-Me_2N, solid.	2 : 3-Me_2N, solid.	2 : 6-Me_2N, solid.	2 : 7-Me_2N, solid.
—	—	698	—	683	—	—	—	—	—
—	—	—	—	—	705	—	—	—	—
724	—	—	—	720	719	—	—	—	—
743	747	755	742	750	752	—	748	—	—
—	774	—	—	—	—	773	—	—	771
786	—	—	—	786	—	789	—	—	—
—	797	797	—	—	—	800	—	—	—
808	—	—	—	814	—	814	—	816	—
—	—	824	—	—	823	—	—	—	—
—	845	—	—	836	—	—	—	—	840
—	859	854	—	—	—	—	—	—	—
865	—	—	—	868	870	—	872	—	—
—	889	—	891	897	897	—	—	886	—
—	948	948	—	—	936	943	948	—	920
966	—	—	968	963	965	971	—	960	—
—	—	—	—	978	975	—	—	—	976
—	983	—	—	—	—	—	—	—	—
998	—	999	—	—	—	—	—	—	—
—	—	—	—	1004	1005	—	—	—	—
—	1010	—	1014	—	—	—	—	—	—
—	1027	1023	—	—	—	—	1023	—	—
1038	—	1034	1035	1038	1036	1040	—	1036	—
—	—	—	1066	1054	—	—	—	—	1048
1083	—	1089	—	1078	1072	—	1086	—	—
—	1131	1139	—	—	1142	1111	1145	—	—
1153	1159	1162	—	1163	1163	1158	—	1163	—
1185	1178	—	1171	—	1196	1167	—	—	1182
1213	1217	1217	1205	1213	1207	—	—	1209	—
1236	(1237)	—	—	—	—	—	1235	1237	1247
1269	1278	1270	1258	1265	1267	1262	1274	1269	1281

Analytical Possibilities.

(a) *Monoalkylnaphthalenes.* The strong bands at 732 and 780 cm^{-1} in the α-substituted and the group of four bands between 1126 and 1170 cm^{-1} in the β-substituted compounds would enable the two classes of compounds to be differentiated, but it would not be possible to determine the length of the side chain. As no compounds with branched side chains were available, the possibility of differentiating branched and straight side chains is not known.

(b) *Dimethylnaphthalenes.* From the abundance of the isomers, the similarity of their ultra-violet spectra, and the extensive overlapping of their infra-red-absorption bands, it is plain that the analysis of mixtures of these isomers by their spectra alone is likely to be a matter of some difficulty.

In this case the method [9, 11–14] is further complicated by possible changes of intensity and frequency of absorption bands during change of state.[15] This difficulty is readily overcome, however, by using solutions in carbon disulphide and carbon tetrachloride of appropriate concentrations and path lengths.

No analyses of synthetic mixtures have been carried out, but if the number of isomers could be limited, for example, as outlined below, there

TABLE III.

Compound.	Methyl bending.			CH_3: (Hydrogen bending).				Aromatic ring.		
Naphthalene (N):										
Solution	—	—	(1391)	—	—	—	—	1507	1592	—
1-MeN:										
Liquid	1381	1397	—	—	—	1436	1460	1512	1599	1630
Solution	1374	1381	—	—	—	1431	1452	1504	1591	—
2-MeN:										
Solid	1374	—	—	—	1423	1455	1466	1525	1595	1625
Solution	1374	—	—	—	1425	1448	1466	1504	1596	1632
1:2-Me_2N:										
Liquid	1371	—	—	—	1416	1433	1465	1513	1611	1638
Solution	1386	—	—	—	—	1442	1471	1512	1596	1622
1:3-Me_2N:										
Liquid	1376	—	—	—	1416	1448	1471	1516	1611	1636
Solution	1378	—	—	—	1414	1442	1460	1518	1609	1628
1:4-Me_2N:										
Liquid	(1394)	—	—	—	1428	1448	1468	1521	1604	—
Solution	1376	—	—	—	1418	1438	1458	1513	1601	—
1:5-Me_2N:										
Solid	1379	—	—	1420	1435	1452	1464	1524	1608	—
Solution	1372	—	—	1402	1418	1439	1464	1514	1602	—
1:6-Me_2N:										
Liquid	1376	—	—	—	1433	1455	1474	1523	1610	1637
Solution	1376	—	—	—	1420	1435	1464	1509	1601	1636
1:7-Me_2N:										
Liquid	1365	—	—	—	—	1447	1474	1517	1611	1643
Solution	1375	—	—	—	—	1435	1463	1508	1598	1633
1:8-Me_2N:										
Solid	1373	1381	—	—	—	1432	1466	1523	1593	—
Solution	1367	1382	—	—	—	1436	1456	1512	1587	—
2:3-Me_2N:										
Solid	1375	—	—	—	—	1433	1460	1510 ?	1605	—
Solution	1372	—	—	—	—	1431	1446	1500	1598	—
2:6-Me_2N:										
Solid	1378	—	—	—	—	1442	1450	1505	1607	1623
Solution	1371	—	—	—	—	1440	1447	1505	1607	—
2:7-Me_2N:										
Solid	1366	—	—	—	—	1437	1455	1512	1609	—
Solution	1370	—	—	—	—	1435	1454	1512	1609	1636

is little doubt that quantitative analyses could be carried out by the usual methods for multi-component liquid mixtures,[11, 12, 13] provided that adequate resolving power could be used.

In general, the ease of detection and estimation of a given isomer will depend on its concentration in the mixture under examination, the complexity of the mixture, and the relative proportion of the other isomers

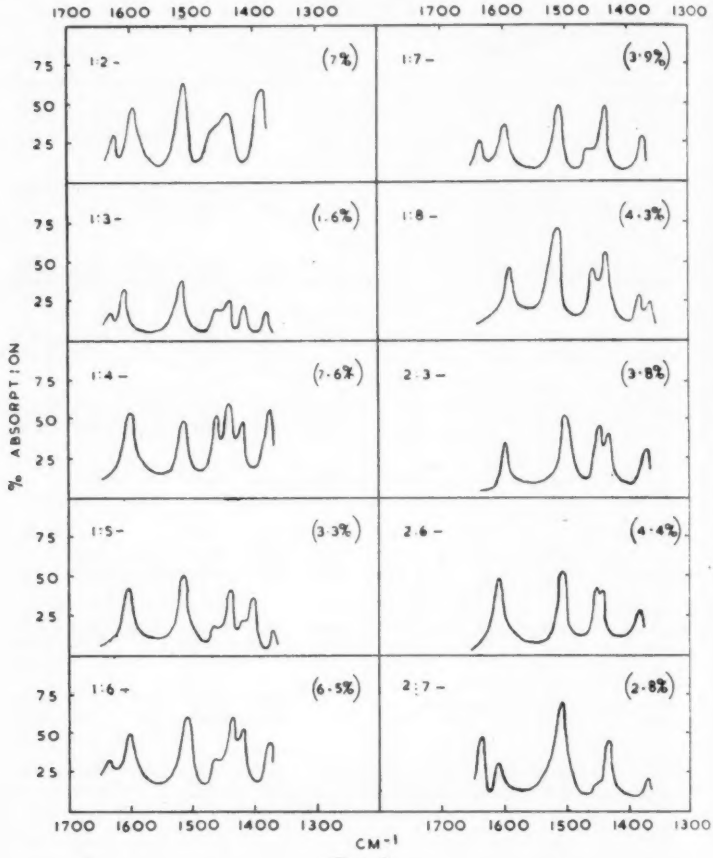

FIG. 3.

THE DIMETHYLNAPHTHALENES IN CARBON TETRACHLORIDE SOLUTION.

present. There are physical and chemical methods which can be used to decrease the complexity of the mixture, such as fractional distillation, fractional crystallisation with or without an added solvent, fractional sulphonation, or fractional hydrolysis of the dimethylnaphthalenesulphonic acids. In general, it may be predicted that if the number of isomers present can be reduced to four a quantitative analysis would be possible.

ACKNOWLEDGMENTS.

The authors wish to thank Dr J. C. Smith of the Dyson Perrins Laboratory, Oxford, for the gift of the hydrocarbons, Dr F. Morton for his

suggestions and advice, and the Directors of Trinidad Leaseholds Ltd for permission to publish this work.

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THE SURFACE TENSION-RULE FOR ASPHALTIC BITUMEN.

By F. J. Nellensteyn (Fellow), and M. Baart.

In the original papers [1] on the surface tension-rule many data on the relation between surface tension and solving power of various liquids are to be found, but in view of new data a revision of the list then given seems necessary. Reference may be made, *e.g.*, to a former paper [2] in which attention was drawn to the fact that the normal petroleum ether asphaltenes contain a certain percentage of compounds which precipitate by non-miscibility. Further, the number of organic liquids controlled for this purpose has been extended considerably and also some inorganic liquids are mentioned. The results are given in Table I.

Comparing this list with the previous one, it appears that the hydrocarbons of the methane series and the petroleum ether have disappeared; these compounds are displaced from the list of flocculents to the non-completely miscible liquids. Many amines, but not all, proved to be miscible with the oily medium and the protective bodies of asphaltic bitumen. Introduction of the amine group into hydrocarbons generally increases the miscibility, but the aromatic amines, aniline, and toluidine are practically not miscible, while benzene and toluene are good solvents for asphaltic bitumen. All the halogens favour the miscibility. Oxygen, especially the –OH and =O groups, decreases the miscibility, but its influence may be counterbalanced by a great number of CH_2 groups (the higher numbers in a homologous series) or by alkylation (ethers, acetals, and esters). The favourable influence of the benzene and the hexahydrobenzene kernel on the miscibility may be partly due to the presence of six CH or CH_2 groups, as noted before. The non-miscibility of the aromatic amines and the opposite behaviour of the aliphatic amines indicate that the influence of the benzenekernel on the miscibility, if present, is only small. This is in contradiction to the opinion of other investigators in this field.[3]

Comparing the complete miscibility of *cyclo*hexane with the opposite behaviour of hexane, it appears that cyclation of CH_2 groups favours the miscibility.

All the aromatics show a surface tension higher than 26, so there are no aromatic flocculents. Among the solvents a great number of aromatic compounds is to be found, but also many aliphatic and inorganic compounds are peptizing agents. Only few oleophile inorganic liquids are to be found; some of these proved to be miscible with the oily medium and the protective bodies of asphaltic bitumen. The peptizing and flocculating properties of these inorganic compounds are in accordance with the surface tension-rule.

In Fig. 1 the amount of precipitate is plotted against the surface tension. The line *AB*, which connects the average amount of precipitate of three liquids, with a surface tension of about 17 dyne/cm, with that of two liquids of 23·5 dyne/cm may be considered as the normal relation between

TABLE I.

Compounds which are completely miscible with the medium and the protective bodies of asphaltic bitumen.	Surface tension, 25° C.	Percentage of precipitate with one asphaltic bitumen.
Flocculating-agents:		
Methylethylether	13·9 *	36·2
Silicontetrachloride	16·2	48·7
Diethylether	16·7	25·0
Di-*iso*-propylether	17·0	27·4
Mono-*iso*-propylamine	17·2	30·8
Diethylamine	18·1	12·1
Ethylchloride	18·8 *	17·8
Acetal	21·0	23·0
n-Propylchloride	21·1	2·3
Dibutylether	22·4	17·6
Monobutylamine	22·9	14·8
Pinacoline	23·0	24·8
Tributylamine	23·3	20·2
Dibutylamine	23·5	2·6
Ethylbromide	23·5	1·1
Amylacetate	24·1	19·9
Intermediate zone:		
Carbontetrachloride	25·4	—
*Cyclo*hexane	25·6	—
Peptizing-agents (solvents):		
Chloroform	26·2	—
Octylalcohol sec.	26·4	20·6
Fluorobenzene	26·5	—
Methylenechloride (1)	27·2	—
Benzene	27·7	—
Xylene (2)	27·8	—
Toluene	28·1	—
Ethyliodide (3)	28·2	—
B.B. dichloroethylether	28·4	—
Methyliodide	29·4	—
Carbondisulfide (4)	30·0	—
Thiophene	30·0	—
Decaline (5)	30·2	—
*Cyclo*hexylamine (6)	31·1 (21°)	—
Tetrachloroethylene	31·2	—
Thymol	32·3	—
*Cyclo*hexanone (7)	32·8	—
Chlorobenzene	32·9	—
Bromotoluene	33·9	—
Ethylbenzoate (8)	34·6	—
Anisol	34·6	—
Pyridine (9)	34·9	—
Piperidine (10)	34·9	—
Tetraline	35·0	—
Benzylacetate (11)	35·0	—
Arsenouschloride	39·0	—
Bromoform	39·4	—
Phenylmustardoil (12)	40·2	—
Orthonitrotoluene	40·6	—
Sulfurdichloride	42·0	—
Nitrobenzene	42·6	—
Quinoline	44·7	—

* These values are calculated from determinations at a lower temperature and the temperature coefficient of allied compounds.

Methylethylether	17·2/−13° C
Ethylchloride	20·6/+10° C

The numbers 1 to 12 correspond with the numbers in the graph.

surface tension and the amount of precipitate for the investigated asphaltic bitumen,* a distillation residue of a Mexican crude with a high asphaltene-content. Other asphaltic bitumens give similar results.

Some flocculents give too high values, others too low precipitates. Although in most cases this does not lead to exceptions; in one case (*sec*-octyl alcohol) a high amount of precipitate has been stated, while the surface tension is above 26, the critical value, although only just above. There are many causes for these irregularities. In the first place the flocculation or peptization is directly caused by the interfacial tension micelle-medium. In Antonow's law for the relation between surface tension and interfacial tension some conditions are posed, which in the

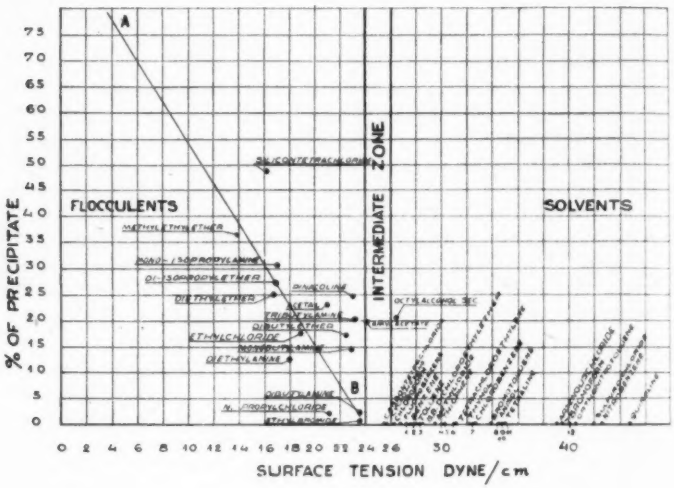

FIG 1.

case of the surface tension-rule are perhaps not always fulfilled. Adsorption of compounds in the immediate neighbourhood of the carbon kernel may lead to higher values of the interfacial tension than indicated by the surface tension of the flocculating liquid. So in the case of too low precipitates this factor may play a part.

An absolute separation of the protective bodies from the carbon kernel is not possible. In the case of the higher amounts of precipitates, incomplete miscibility, which could not be proved by the ordinary methods, must be considered as the most probable cause of these irregularities.

As a matter of fact the liquids above the line *AB* contain groups, which are unfavourable for miscibility. The presence of incompletely bituminized compounds, the so-called *difference asphaltenes*, which possess miscibility

* Softening point (R. & B.) . . . . . 60·3° C
Penetration (25° C, 100 g, 5 sec) . . . . . 30·7
Flash point (open) . . . . . 307° C
Loss on heating (5 hr at 163°) . . . . . 0·1%

properties different from those of the ordinary hydrocarbons, must also be taken into account.

M. Duriez [4] applying the surface tension-rule to coal tar succeeded in deducing an equation which enables us to calculate the amount of precipitate from the surface tension and a parameter for the kind of tar. This different behaviour of coal tar is due to various factors. In the first place tar contains particles of widely varying diameter. Therefore the precipitate–surface-tension line shows no angle at the critical point, but for all surface tensions a certain amount of precipitate is found. This gives a more regular curve. Secondly, the particles of the tar as a whole are coarser than those of the asphaltic bitumen, which only contains ultramicrons. In the tar micelle the adsorption phenomena which may cause irregularities are not so pronounced with tar as with asphaltic bitumen. Another application of the surface tension-rule has been found by Kreulen.[5]

Conclusion.

The investigations on the surface tension-rule have been extended to a great number of organic liquids of various character and to some inorganic liquids. As a whole these results are satisfactory, as well for the organic as for the inorganic liquids, only one serious anomaly having been found. The quantitative results are not so good, in contradiction to those obtained with coal tar. The reasons for this different behaviour are explained.

State Road Laboratories,
The Hague, Holland.
January 1949.

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[2] *J. Inst. Petrol.*, 1940, **26**, 404–406.
[3] Pfeiffer, J. Ph., and van Doormaal, P. M. *J. Inst. Petrol.*, 1936, **22**, 435.
[4] Duriez, M. *Ann. Ponts et Chaussées*, 1938, **108**, 403.
[5] Kreulen, D. J. W. "Elements of coal chemistry," Rotterdam, 1948, p. 180.

OBITUARY.

DR FRIEDRICH BERGIUS.

WITH the death of Dr Friedrich Karl Rudolph Bergius at Buenos Aires in his sixty-fifth year, the world has lost an outstanding research worker and pioneer in the application of science in industry, particularly in the field of high-pressure chemical reactions.

It might be said that Bergius was born in a chemical atmosphere, for his father owned a chemical factory in Goldschmieden, which was among the first to successfully manufacture alumina; there is little doubt that the opportunity which Bergius had there of studying technical chemistry was of great value to him in later life.

His keen interest in high-pressure technique began with his period of post-graduate study in 1909 at Kahlsruhe, where he investigated gaseous equilibria, especially those involved in the synthesis of ammonia. In 1910 he set up a private technical research laboratory in Hanover, where he was Professor at the Technical High School, and where he extended his investigations on the effect of high pressure on a variety of chemical reactions. This work included an examination of the effect of heating cellulose and peat with water under pressure, and from these experiments he succeeded in producing a coal-like substance or "artificial coal." Then came the idea that it might be possible to convert these artificial coals into hydrocarbons and water by treating them with hydrogen under pressure, an idea which was fully confirmed by experiment. The enquiry was immediately extended to include natural coal; and in 1913, in collaboration with his colleagues Specht and Billwiller, he developed the coal-liquefaction process, as it was then called. This is the discovery by which Bergius will ever be remembered. In 1916 a plant was erected at Mannheim-Rheinau for the continuous hydrogenation of coal at 200 atmospheres pressure and at 400° to 500° C. As was no doubt expected, many difficulties were encountered in this new venture, but these difficulties were steadily overcome and full technical success was ultimately achieved. The first commercial plant for the hydrogenation of coals to produce oils was that built by the I.G. Syndicate at Leuna in 1927. With subsequent developments this plant reached by 1945 an output at a rate of more than 600,000 tons of liquid products per annum.

The importance of the Bergius process of hydrogenation and its possibilities were fully recognized in Great Britain shortly after the 1914–18 war. A few years later an option on the patent rights was obtained for the British Empire. By 1926 preliminary experimental work was in progress at the Fuel Research Station at Greenwich where a pilot plant was erected to study the application of the process to British coals and British coal tars. Imperial Chemical Industries, Ltd., also undertook extensive investigations, and by 1935 they brought into operation at Billingham a plant for the hydrogenation of British bituminous coal. This plant, which has since been used mainly for the hydrogenation of creosote, has provided more than

100,000 tons of motor spirit a year. Some idea of the magnitude of the scale of operation of the hydrogenation process is given by the fact that by 1944 there were in Germany eighteen hydrogenation plants of various kinds with a total capacity in the region of 4 million tons of oil a year.

With the successful development of the hydrogenation process on a manufacturing scale, Bergius turned his attention to another problem in which he had been interested for some years. That problem was the possibility of conversion of cellulose in the form of wood into sugar. With his previous experience, he applied high-pressure technique to that problem and, such was his resourcefulness and ingenuity, that he brought it to a stage of manufacturing operation.

The outstanding value of Bergius' achievements received world-wide recognition by many awards, including the Nobel Prize for chemistry in 1931, and in Great Britain the Melchett Medal of the Institute of Fuel in 1934. In addition, he was the recipient of honorary degrees of several universities in different parts of the world.

ROBERT PITKETHLY.

It is with deep regret that we have to record the death, on March 6, 1949, of Robert Pitkethly, who was in his seventy-first year.

Receiving his technical education at the Glasgow and West of Scotland Technical College under Prof. G. G. Henderson, he afterwards worked for about a year with Messrs James Black & Co., Ltd., calico printers, Dumbartonshire, and then for a further eight years with Messrs Bryce and Rumpff, chemical merchants, Glasgow, in which firm his father was a senior partner.

In 1906 he turned his attention to petroleum and, joining the Burmah Oil Co., Ltd., went as a chemist to Syriam.

He was appointed refinery manager, first at Yenangyat at the beginning of 1909 and then at Syriam, from where he left for Iran in May 1910, becoming the first works manager of the new Abadan refinery in 1911. He was invalided home for a few months in 1914, returning to Burmah until 1919, when further serious illness, lasting for some time, led to his final retirement from Eastern activities.

"Old Pit," as he was affectionately known to his many friends, was appointed as chemist at the Sunbury laboratories of the Anglo-Iranian Oil Co., Ltd., early in 1923, and during 1924 he was engaged for some months in Broxburn and Uphall on experimental work on the Auld–Dunstan–Herring cracking plant. In 1935 he was transferred from the laboratory to the managerial staff at Sunbury.

Pitkethly was admitted as a Freeman of the Burgh of Glasgow in 1907. He was elected a member of the Institute of Petroleum in 1923 and transferred to Fellow in 1939.

He is survived by his widow and three sons, to whom we extend our deepest sympathy.

R. S.

CORRESPONDENCE.

"*Emulsions of Sea Water in Admiralty Fuel Oil with Special Reference to their Demulsification.*"

To the Editor, *Journal of the Institute of Petroleum.*

SIR,

Dr Lawrence, in his letter of February 2,* has rather missed the point. Bearing in mind, as he says, that the original contribution was "a serious scientific paper," we were surprised (to put it mildly !) that the opening sentence made a statement which, we suggested, was not confirmed in practice.

We can perhaps leave it to your readers to imagine the chaos which would result if "all present-day fuel oils" were to emulsify so readily as the authors stated in their damning opening remark. Remember that scores of millions of tons of stable, non-emulsified fuel oil are used annually by satisfied customers world-wide.

Fortunately, Dr Lawrence has the grace now to admit in his letter that "formation of sludge requires, first, contamination by a large amount of water and the sedimentation of the emulsified water to form the close-packed emulsion which is sludge. This process, as pointed out in the paper, proceeds very slowly."

We are content to leave it at that.

Yours truly,
For THE SHELL PETROLEUM COMPANY LIMITED
H. E. G. MUMFORD

St. Helen's Court,
Great St. Helen's,
*London, E.C.*3.

March 25, 1949.

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* See page 219.